THE WATER-SOLUBLE GUMS

BY

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Preface

This volume is an attempt to coordinate information relating to the water-dispersible products derived largely from a wide variety of plants and known as gums. Applications in the arts have been established for centuries. The collection, trade, and usage in some cases date from Biblical times.

In some of the author's technical activity there was a need for clarification of the confusion in gum designation and technology, as well as definition of the concept of the term "gum" so often misapplied and misused.

Practice and art are ahead of science in the gum field. An effort has been made to bring them more closely together. The author has been aided in this work by Dr. Z. C. Loebel and Mrs. Isabelle Suarez Magranet who explored the chemical literature, Mr. Frank M. deSanta who carefully prepared the manuscript, and Miss Edna M. Rogers who in innumerable ways helped complete the job.

Thanks are rendered to Dr. Charles R. Toothaker of the Philadelphia Commercial Museum, T. M. Duché and Sons, Inc., of New York, The Fish and Wildlife Service of the Department of the Interior, and the Department of Commerce of the United States Government for various illustrations in the text.

It is hoped that this volume will be of service to those in the field of gum technology and stimulate work by others to bridge the gaps between art and science. Inasmuch as the ramifications of the subject give rise to errors and workers in the field disagree, constructive suggestions and criticisms will be most welcome.

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Chapter 1

Classification and Chemistry of the Gums

The so-called "water-soluble" gums have been articles of commerce from Biblical times. Commercially the term embraces a group of substances whose properties of forming viscous adhesives, jellies, or pastes, have earned a place for them in the arts and industries.

The designation of "water-soluble" gums is a misnomer in many ways, as the materials are not soluble in the strictly scientific sense as salt, sugar, and other crystallizable materials are soluble; the gums are not crystalloids but colloids. They do not show crystal form, but are in the strict sense amorphous; they have neither melting point nor freezing point nor boiling point characteristics. They are organic substances of indefinite composition as they appear to be complexes associated with plant life processes.

The appellation of "gum" in commerce is very wide and confused in its application. Often the term is employed for materials which affect the senses of touch, taste, and sight in a measure summed up as a property of "gumminess." It is difficult to define, but visual and manual examination of a material may cause the observer to call it a gum.

In this volume the term "gum" will be limited to the tree exudations of which arabic, ghatti, karaya, and tragacanth are examples; the seaweed colloids represented by agar, Irish moss, carrageenin, and the alginates; the seed extracts of which locust bean, locust kernel, and quince seed gums are typical; the manufactured dextrins and British gums, and the water-dispersible derivatives of cellulose which are industrial competitors of the older established materials. Inasmuch as gelatin has many gum uses, a discussion of this protein is included.

These materials are all water-loving colloids—they may apparently dissolve, but actually disperse or swell or absorb water to form commercially valuable and interesting substances. They are hydrophilic and organic-solvent phobic. The resinous materials in contrast to the gums are hydrophobic and organic-solvent philic.

In the wider sense many proteins are gums and industry-wise find applications alongside of and in a manner similar to the materials dealt with in this volume. The literature on glue, gelatin, and casein is extensive. There exist a number of exhaustive treatises and monographs. An analogous situation exists in the case of the starches and related carbo-

hydrates. Other than gelatin and the colloid theory of the proteins, these materials are therefore omitted from the "gum" discussion, as their inclusion in this volume would add little to the existing knowledge. Gelatin, however, is water-dispersible and therefore might be considered a gum. Other proteins are dispersible only with alkalies or alkaline materials and therefore are not gums and are excluded from this volume.

In contrast to the ordered information on the protein materials, coordination of the scattered knowledge, often of contradictory nature, on the gums is definitely needed. This volume attempts the task of such integration in a field where the trader, merchant, and artisan for centuries have been ahead of the chemist, the botanist, or the engineer. Scientific integration may remove some of the confusion and mystery and render the workings of the "practical" operator more understandable and susceptible of progress.

The hundreds of names of the natural gums denote the geographical areas in which they are gathered, the districts and ports of wholesale collection and the points at which they enter commerce, the grading and distribution centers. Such nomenclature inevitably leads to confusion, omitting that intentionally caused by traders for their own advantage. The terminology needs simplification. In this volume the natural gums will be treated in the groups originating with specific species of trees or plants. There are chapters therefore devoted to gums from the Acacia species of trees (gum arabic as an example), the Anogeissus species (ghatti as a typical one), the Astragalus species (which is the source of tragacanth), the Prunus species (from which cherry gum is derived), the Sterculia species (with karaya as a specific case), with a general discussion of the other species from which commercially unimportant quantities of gum enter world trade. The gums from the same species of trees are chemically similar in that the same components are found, while gums from different species differ chemically and physically.

In this volume an attempt will be made to employ the term "gum" as a generic name for a class of substances organic in nature and related to the sugars and the carbohydrates. These gums are uncrystallizable and are usually composed of carbon, hydrogen, and oxygen in the main. They occur widely in plants and to a limited extent in animals. They are gums in that they have the characteristic property of forming viscous solutions or mucilages either by "dissolving" in water or by absorbing many times their own volume of that solvent. The term "dissolving" is employed advisedly inasmuch as colloidal solutions are formed rather than the true solutions of crystallizable materials such as formed from salt (sodium chloride) or sugar (sucrose).

Commercial gums contain more or less mineral matter, chiefly calcium,

magnesium, and potassium. Nitrogen is often present but is not considered an essential constituent. In this sense the true gums differ from the proteins, of which nitrogen is an essential component.

Those tree exudations which find employment in the paint, varnish, and lacquer industries are often referred to as gums. Thus, for example, there are gum rosin, gum copal, gum damar, and many others. These are the "natural resins."[1] The "gum" appellation to resins is distinctly a misnomer, as in strict terminology the gums are related to the sugars and the carbohydrates. Gums are colloidally soluble or dispersible in water, forming viscous solutions, and they are insoluble in drying oils and organic solvents. On heating, they decompose completely without melting, usually showing charring. In contradistinction, natural resins are insoluble in water. They show more or less solution in organic solvents and vegetable oils. They are chemically related to the terpenes or the essential oils. When heated, the resins melt with distillation of volatile oils as the temperature is increased. They do not show a "carbonizing point," nor do they produce coke when destructively distilled. Gums are totally unrelated to resins either physically, chemically, or application-wise.

The true gums are roughly divisible into three classes: (a) soluble gums, typified by those produced in the Anglo-Egyptian Sudan and in Senegal, which dissolve in water, forming transparent solutions; (b) insoluble gums represented by tragacanth gum which absorbs the aqueous medium, swells into a jelly, and finally on addition of sufficient water breaks down into a very thick transparent solution; (c) half-soluble gums such as "Persian insoluble gum" which is intermediate in its properties. It partially dissolves in water to form a swollen jelly which on the addition of more water also passes into solution.

Soluble gums are applied to a great number of purposes in the arts. The finest and least-colored varieties are employed in the clearing of liqueurs, the "finishing" of silk, and in the preparation of fine water colors. Other grades find application in confectionery and pharmacy, in sizing, printing, and the finishing of textiles, and the treatment of paper, as well as in certain dyeing processes. The least costly varieties are used in the manufacture of stationery, matches, inks, and commercial emulsions.

In general, the gums originate in portions of the African Continent as the Sudan (Sudan or Kordofan gum); the forest of the Blue Nile (talh or talha gum); the French Colony of Senegal (Senegal gum); Northern Nigeria (gum arabic); Morocco ("Morocco," "Mogadore," "Brown Barbary" gum); Tripoli (gum arabic); Tunisia (gum arabic); Tangan-

[1] C. L. Mantell, C. W Kopf, J. L. Curtis, and E. M. Rogers, "The Technology of Natural Resins," John Wiley & Sons, Inc., New York, 1942.

yika (gum arabic); Southwest Africa (acacia); Cape Colony, Orange River Colony, Somaliland, and Abyssinia (Aden and East Indian gum); in portions of Asia, as India and adjacent countries (ghatti and karaya gum); in Asia Minor, Kurdistan, and Iran (tragacanth); Australia (wattle gum); South America, where the usage is mostly local, and to a small extent in Europe (cherry gum). The seaweed colloids, agar, Irish moss, and the alginates are derived from marine products gathered off the coast of Japan, the east and west coasts of the United States, the marine areas of the British Isles and Europe, and the shores of the Atlantic and Pacific Oceans. The processed carbohydrates such as the dextrins and British gums are derived from American starches such as corn and potato, as well as tapioca from the Netherlands Indies. The hemicelluloses are from seeds of trees and plants from Europe, Persia (Iran), the Argentine and the United States. Gelatin is ordinarily derived from animal sources in the United States. The synthetic competitors of the gums such as the processed celluloses are from native or Canadian wood pulp or American cotton linters.

As shown in Fig. 1, the gums are obtained by tapping or collecting from trees and shrubs, separation from marine plant life, by milling from some seeds or extraction from others, thermal treatment of starches from kernels or root crops, chemical processing of cellulose from trunks of trees or from the cotton plant, as well as separation of animal by-products and purification procedures.

With the exception of the proteins, whose chemistry has been the subject of much study and whose colloid behavior is in many respects related to them, the gums are carbohydrates which upon hydrolysis yield various saccharides or sugars.

Colloidal Behavior of the Gums. The gums in general swell in water to form viscous solutions. The affinity for water exhibited by gum arabic is not characteristic of all the other gums; nevertheless water is the solvent common for all the gums. The degree of solubility and swelling varies to some extent.

The viscous solutions obtained from the gums are colloidal in behavior, exhibit swelling pressures, form gel structures at extremely low concentrations and over a wide concentration range. The gums are highly selective insofar as the solvents are concerned. Gum arabic and gelatin, for instance, exhibit an extraordinary affinity for water, yet are insoluble in most organic solvents. The colloidal solutions manifest low surface tension, do not crystallize, and act as protective colloids and stabilizing agents.

Water-peptizable colloids like gelatin, gum arabic, dextrin, soap, or saponine will peptize many precipitates. They are often called protective

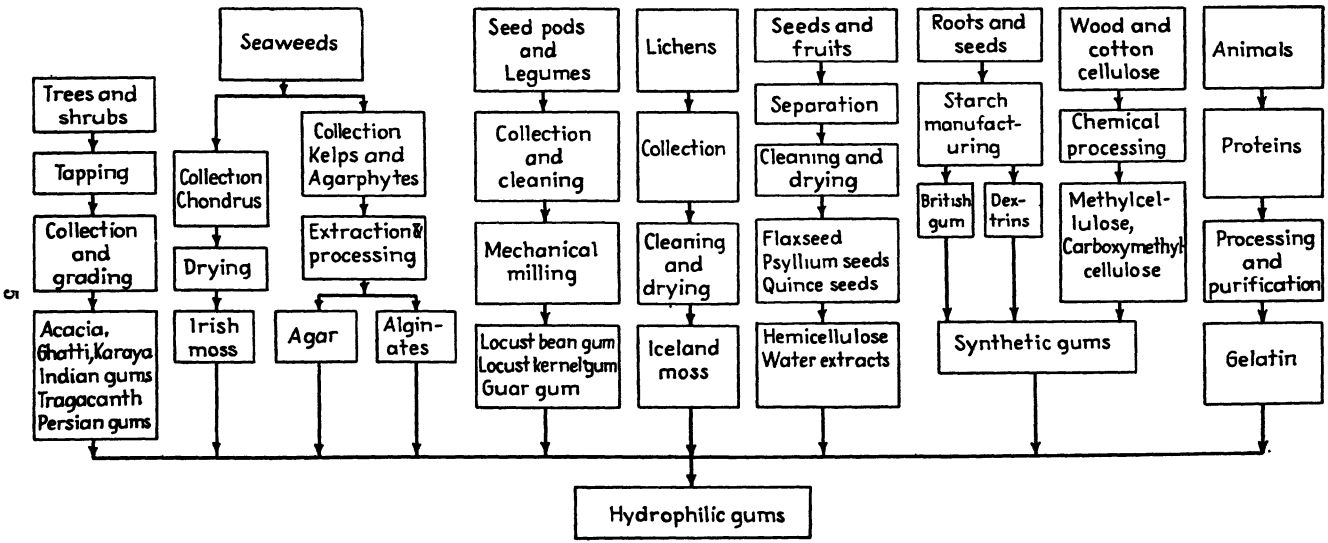


FIGURE 1. Source and derivation of gums.

colloids because they prevent the agglomeration and consequent settling of finely divided particles or precipitates. Casein is not peptized by water, but acts as a protective colloid when peptized by acids or alkalies.

All these properties make the gums extremely valuable in manufacturing processes. The textile, cosmetic, pharmaceutical, and food industries have found wide application for them. The paper and paint fields have utilized some of the gums, but to a lesser extent.

Colloid chemistry is a vast field in itself, and has been extensively covered in the literature. No attempt will be made to correlate all the data available, but only those sections which deal specifically with the colloidal behavior of the gums will be incorporated in this book.

The gums belong to that class of colloids called emulsoids which form hydrophilic "water-loving" dispersions; those which are "water-fearing" are hydrophobic in nature. The resins fall into this group. The gums swell or disperse in water, and they generally tolerate the presence of large amounts of electrolyte. The gums form highly viscous solutions or absorb large quantities of water in order to swell.

Agar is an emulsoid similar to gelatin in many respects. It has a higher jelly strength at a given concentration, a higher gelation range, and is less sensitive to changes in pH.

The term "gels" has been used to cover a wide variety of conditions which is often confusing; it has sometimes been used to designate amorphous bodies. In this book its use will be restricted to denote transparent or translucent bodies containing a considerable proportion of liquid, but maintaining shape and exhibiting rigidity. The word "gel" is also used to include jelly which differs from a gelatinous precipitate in that no supernatant liquid is present where the jelly is first formed. It is really the general term for a solid or semi-solid colloid. Jellies of agar and gelatin are regarded as gels because they are heat-reversible. Heat-reversible gels are converted into sols (apparent but not true solutions) by heating and the sols may in turn be converted to gels by cooling. The change from a gel to a sol is peptization. This term has not become too popular; coagulation, agglomeration and agglutination appear to be more accepted.

The majority of readers assume that gels are two-phase systems: The accepted structure for gels of hydrophilic colloids to which the gums belong is a mass of intertwined fibrils, enmeshing the solvent or dilute solution as well as binding the liquid of the solution. The filaments are composed of adhering particles. This is then a two-phase, solid-liquid structure, both phases of which are continuous.

Lewis, Squires, and Broughton[2] define "gel" as a mixture, one com-

[2] W. K. Lewis, L. Squires, and G. Broughton, "Industrial Chemistry of Colloids and Amorphous Materials," The Macmillan Co., Inc., New York, 1942.

ponent of which is fluid, homogeneous down to substantially colloidal dimensions and capable of resisting a shearing force.

Katz[3] concludes that gelatin is a crystallization phenomenon on the basis of crystal interference rings revealed by x-ray examinations of agar and gelatin gels. This confirms Bradford's belief.[4]

Colloidal dispersions are known as sols. Certain sols change to semi-solid, jelly-like masses called gels upon partial evaporation of the dispersion medium by a decrease in temperature or by the addition of other chemicals. Upon complete dissociation of a sol or gel, a solid residue results, which may be transparent and glassy in appearance or porous and sponge-like, or an amorphous powder.

Dried gums generally redisperse in water and are sometimes referred to as gels.

Sols of the hemicellulose type,[5] such as locust bean, Iceland moss, quince seed, and psyllium seed, show a high viscosity, increasing enormously with the concentration, but heat has only a slight effect in decreasing it.

Jellies[6] form from a colloidal solution providing a suitable amount is precipitated at a suitable rate without agitation. The absence of a medium that exerts an appreciable solvent or peptizing action is another requirement. No jelly or only a very soft jelly results if the concentration of the colloid is low. Contraction is likely to occur if the precipitation velocity is too great, and results in the formation of a gelatinous precipitate instead of a jelly. Bancroft states that, theoretically, a jelly may have a structure varying from a granular mass through interlacing threads to some sort of mesh work.

Some writers[7] believe that the principal difference between a sol and a gel is the elastic properties of the latter. Investigations of the elastic constants of gelatin gels show that they are perfectly elastic for small stresses applied over short periods. The volume remains unchanged even for a considerable deformation. The stress required to maintain a given deformation decreases with the duration of application, but does not become zero, *e.g.*, the gel shows relaxation which does not become complete; the optical anistropy (double refraction) produced by the stress does not decrease with it but remains at the value corresponding to the first application of the stress.

[3] J. R. Katz, *Rec. trav. chim.*, **51**, 513, 835 (1932).
[4] Bradford, *Biochem. J.*, **21**, 351 (1918).
[5] "First Report on Colloid Chemistry and Its General and Industrial Applications," p. 63, British Assoc. for the Advancement of Science, His Majesty's Stationery Office, London, 1917.
[6] W. D. Bancroft, "Applied Colloid Chemistry," p. 336-7, McGraw-Hill Book Company, Inc., New York, 1932.
[7] *J. Chem. Soc.*, **117**, 1506 (1920); *Proc. Roy. Soc.* (London), **98A**, 395 (1921).

Alexander[8] explains the transformation of a sol to a gel using a cooling gelatin solution as an example. He states that, as the temperature decreases, and thermal agitation diminishes, the finely dispersed gelatin particles are reduced in their kinetic energy or Brownian motion, and then mutual attractive forces begin to assert themselves. This results in the formation of secondary colloidal particles which with gelatin are elongated or thread-like. This is especially true if the solution is sufficiently dilute. The viscosity or internal friction increases as the chains grow and become tangled with each other until finally all of the fluid is enmeshed in the growing tangle or else becomes a part of it.

If the sol-to-gel transformation can be repeated in gels by a suitable choice of conditions, then they are considered as "reversible" gels. If, after setting, reliquefaction is not possible other than by indirect means, these are called "irreversible gels." The irreversible gels are most frequently of the emulsoidal type.

The viscosity[9] of a liquid is the resistance offered to shearing, to stirring, or to the flow through a capillary tube. The viscosity coefficient is the force required to move, at unit velocity, a plate of unit surface separated from another plate of the same size by a layer of liquid of unit thickness. Bancroft found that in the case of a water-soluble colloid, the viscosity may increase enormously with concentrations; a 1 per cent solution of agar formed a solid jelly. The viscosity of the gums is appreciably affected by temperature.

On cooling, the viscosity of agar and other gums[10] increases to a point at which, and beyond which, no viscosity measurements are possible.

Alexander[11] found that by using powdered karaya gum, the growth of viscosity with the swelling of the gum particles was visible to the naked eye, providing gum of about 80 mesh is used in a concentration of about 2 per cent gum and 98 per cent water. As hydration and swelling occurs among the particles, the amount of free water which acts as a lubricant or separator between the particles steadily decreases, and the viscosity therefore increases. A jelly is formed which is plastic in nature when higher concentrations of gum are utilized.

The viscosity of gum tragacanth[12] is said to be lowered by heating under pressure. It shows only a slight osmotic pressure; a 0.72 per cent

[8] J. Alexander, "Colloid Chemistry, Principles and Applications," 4th Ed., p. 146, D. Van Nostrand Company, Inc., New York, 1937.

[9] W. D. Bancroft, "Applied Colloid Chemistry," 3rd Ed., p. 237, McGraw-Hill Book Company, Inc., New York, 1932.

[10] *J. Chem. Soc.*, 117, 1506 (1920).

[11] J. Alexander, "Colloid Chemistry, Principles and Applications," 4th Ed., p. 147, D. Van Nostrand Company, Inc., New York, 1937.

[12] "First Report on Colloid Chemistry and Its General and Industrial Applications," p. 58, British Assoc. for the Advancement of Science, His Majesty's Stationery Office, London, 1917.

solution gave a pressure of 5 mm. at 17°C., with a parchment paper membrane.

Syneresis is the name given to the process of contraction of gels and the resulting exudation of liquid from the gel. Alexander[13] states that this can be seen when a sheet of dry gelatin is heated above 120° for a while. It becomes insoluble in water, though it still swells to a certain extent. He believes that its constituent particles have approached so closely that the attraction they have for water can no longer force them apart. These particles approach each other so closely after the gel stands that a clot is formed and liquid is exuded, while the clot shrinks.

Thixotropic gels are gels which upon shaking or stirring become sols and the latter on being allowed to remain undisturbed become jelled again. Such gels possibly contain fibrils orienting in an entangled meshwork which upon agitation are disentangled.

Many of the gums, *e.g.*, gum arabic, gum tragacanth, gum karaya, alginic acid, alginates, and locust bean gum, are utilized as creaming agents for rubber latex. Kraemer[14] states that latex and latex cream are thixotropic systems.

Freundlich[15] and Hamaker[16] have submitted a theory on thixotropy in which they suppose that the London-van der Waals forces which are found on the surface of a particle, take a path which causes the particles to hold together reversibly when they are at comparatively great distances from the surfaces. High viscosity is produced by this reversible bond. The particles are torn loose from each other by mechanical agitation. This then permits the particles to move or slide freely along one another which is plainly seen in the resulting reduced viscosity.

Bancroft[17] found that the rate of diffusion of electrolytes in a dilute gelatin solution is very nearly the same as in pure water providing the jelly is not made more concentrated. Other investigators found that the electrical conductance of gelatin solutions is less than in water.

Isocovesco[18] found that the diffusion of colloids may be attributed partly to the adsorbed material. The Brownian movement of the particles also produced diffusion because the bombarded molecules of the medium tend to produce an even distribution of the suspended particles, except where gravity, surface tension, and electrical stresses interfere.

[13] J. Alexander, "Colloid Chemistry, Principles and Applications," 4th Ed., p. 147, D. Van Nostrand Company, Inc., New York, 1937.
[14] E. O. Kraemer, "Advances in Colloid Science," Vol I, pp. 248, 265, Interscience Publishers, Inc., New York, 1942.
[15] H. Freundlich, "Thixotropy," p. 19, Paris, 1935.
[16] H. C. Hamaker, *Rec. trav. chim.*, **55**, 1015 (1936); **56**, 1727 (1937).
[17] W. D. Bancroft, "Applied Colloid Chemistry," 3rd Ed., McGraw-Hill Book Company, Inc., New York, 1932.
[18] Isocovesco, *Biochem. Z.*, **24**, 53 (1910).

Tice[19] differentiates between a dispersing and stabilizing agent. He states that a dispersing agent favors the dispersion of oil into fine droplets, while a stabilizing agent acts protectively to prevent coalesence. Gelatin is considered a stabilizer and not a disperser. The permanency of an emulsion is owing almost entirely to the stabilizing power of the colloid. Emulsifying efficiency is dependent upon the extent of charge of the gelatin employed, coupled with the degree of hydration. This varies directly as the pH departs from the isoelectric point.

Many colloids are said to obtain their stabilizing charge by self-ionization and may be called colloidal electrolytes. Gum agar, soap, clays, and many dyestuffs may be said to belong to this type.

Surface tension may be defined as the force exerted in the plane of the surface per unit length taken perpendicular to the direction of force. Zlobicki[20] found that the addition of 0.5 to 0.8 g. of gelatin to 100 cc. of water causes a marked decrease in the surface tension of the water, while the addition of further amounts has practically no effect. He also found that gum arabic when added to water increases the surface tension within the same limits. Du Noüy[21] has disputed this.

The surface tension of sols that are water soluble is lower than that of water, and these are useful as emulsifying agents. All the gums find application as stabilizers of emulsions.

Hysteresis is the tendency of a body to lose its energy or effect when the force acting upon it is changed in direction. Agar exhibits high hysteresis in the gelation process. To liquefy the gel, it must be heated to well above the temperature at which gelation occurred.

A hydrophilic sol is said to be entirely stable providing it travels neither to an anode nor cathode in an electric field. This factor shows it does not possess a net electric charge. The addition of small amounts of magnesium sulfate or chloride on an aqueous agar sol produced a sharp drop in viscosity identical for the two salts in equal molal concentration. Lewis, Squires, and Broughton[22] believe that this is the result of neutralization of the charge on the agar particles by the magnesium ion.

Solutions of high molecular weight materials, of which the amorphous solids constitute a great percentage, exhibit three flow characteristics which differentiate them from ordinary liquids. First these solutions give viscosities comparable to the solvent utilized, which even in dilute solutions are high. Lewis, Squires, and Broughton[23] cite an example based on this

[19] L. F. Tice, *Drug and Cosmetic Ind.*, **38**, No. 5, 635-6 (1936).
[20] Zlobicki, *Bull. Acad. Sci. Cracovie*, 497 (1906).
[21] Du Noüy, *Colloid Symposium Monograph*, **3**, 25 (1925).
[22] W. K. Lewis, L. Squires, and G. Broughton, "Industrial Chemistry of Colloidal and Amorphous Materials," The Macmillan Company, New York, 1942.
[23] *Loc. cit.*

characteristic, which consists of viscosity comparisons of 1 per cent solutions of sugar, colloidal sulfur, or rubber latex, and agar, starch, and rubber. The first group have viscosities which are only 3 to 4 per cent higher than that of the solvent. The latter have, in the case of starch, a 50 per cent higher viscosity value, 500 per cent in the case of agar and over 1000 per cent for the rubber solution.

Secondly, the viscosity of the solution may vary greatly with the rate of shear; and finally, even dilute solutions often set to gels under the proper conditions.

Gum arabic solutions[24] show a high osmotic pressure, which remains constant over a long period. A pressure of 7.2 cm. of mercury, using a 1 per cent solution of arabic and a copper ferrocyanide membrane, was recorded. An 18 per cent solution gave an osmotic pressure of 120.4 cm.

Moore and Roaf[25] and Edie[26] using a parchment paper diaphragm found, for 6 per cent solutions, pressures of 114 to 170 mm., and for 10 per cent solutions 276 mm. These high pressures which remain almost constant have not been explained; they may be due to the slow diffusion of the electrolytes associated with the carbohydrates, or they may be swelling or imbibition pressures.

Clayton[27] found that gelatin is an excellent emulsifying agent for oils of glyceride and hydrocarbon nature.

Briggs and Schmidt,[28] and Holmes and Child[29] have made detailed studies on the emulsification of benzene in water using gelatin.

Data on the emulsification of arachis and cottonseed oils in aqueous gelatin solution were made by Clayton.

Gum acacia, gum tragacanth, casein, Irish moss, egg-yolk, and saponin have been utilized in pharmaceutical preparations, and these have been studied by many investigators.

Emulsions of benzene in water, using hemoglobin, lacmoid, pepsin, peptone, and dextrin were prepared by Newman.[30]

Bhatnagar[31] studied emulsions of kerosene in water using casein, albumin, and lecthin as emulsifiers.

The chemistry of the individual gums is discussed in specific relation to each specific group in the separate chapters. Despite their chemical

[24] "First Report on Colloid Chemistry and Its General and Industrial Applications," p. 55, British Assoc. for the Advancement of Science, His Majesty's Stationery Office, London, 1917.
[25] Moore and Roaf, *Biochem. J.*, **2**, 39 (1908).
[26] Edie, *Report No. 4, Sudan Gov., Agr. Research Service, Khartoum, Sudan.*
[27] W. Clayton, "The Theory of Emulsions and their Technical Treatment," 2nd Ed., P. Blakiston's Son & Co., Philadelphia, Pa., 1928.
[28] T. R. Briggs and H. F. Schmidt, *J. Phys. Chem.*, **19**, 484 (1915).
[29] H. N. Holmes and W. C. Child, *J. Am. Chem. Soc.*, **42**, 2049 (1920).
[30] F. R. Newman, *J. Phys. Chem.*, **18**, 45 (1914).
[31] S. S. Bhatnagar, *J. Chem. Soc.*, **119**, 1760 (1921).

kinship, each gum is of such a nature that they are not mutually compatible. They may blend in some cases to supplement their properties; at other times they may precipitate each other with lessening of valuable characteristics. Their reaction to specific chemical reagents may be sufficiently different to allow the development of qualitative analytical schemes to detect their presence and identify them. The evaluation of a particular gum in commerce is often of a compromise nature, taking into account purity, general properties, price in the market, and replaceability by other materials, as well as the status of world markets. Many of the gums are imported products from countries whose manufacturing viewpoint is much less developed than that of the United States. These gum-producing countries are often predominantly agricultural. Non-uniformity from crop to crop, or gathering to gathering is a disadvantage, but chemical, mechanical, or solution processing to achieve uniformity to date finds little place. More often than not the tree and shrub exudation gums are finely ground and their impurities are thus temporarily hidden. The processed seaweed colloids are essentially manufactured products and show a high degree of reproducibility as do the milled hemicelluloses or the gelatins.

Some of the gums such as arabic have been a favorite subject of chemical investigation; others in contrast have received little attention. Much of the basic colloid theory applicable to the gums has been developed in connection with the proteins. For this reason some of the general theory is discussed in connection with the proteins and this theoretical aspect is thought to be sufficient excuse to include a section on proteins. This is furthered by the comparative position of gelatin in various gum applications, as well as the increasing competition offered by the seaweed colloids to gelatin in certain fields. Each of the gums finds specific application where others neither replace nor supplement; each has earned its place either over thousands of years or in a short space of time after it reached a commercial production stage. While related chemically, the different classes of gums are definitely individual and distinct.

The gums consist primarily of compounds of carbon, hydrogen, and oxygen of the types related to the starches and sugars, a group which the organic chemist calls carbohydrates. These are commonly associated with plant life processes, so that it is not unexpected that the gums from tree exudations, seaweeds, fruits, and seeds are composed of carbohydrates and their derivatives. Cellulose is also a carbohydrate and thus the constitution of the gums and that of their synthetic competitors, derived by chemical processing of cellulose, are definitely related.

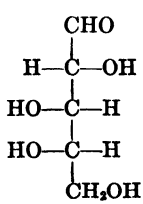
The carbohydrates, although composed of only three elements, are very numerous owing to the differences caused by the spatial arrangement

of the atoms in the molecule. The relative positions of the carbon atoms to each other in three-dimensional space, and the positions of the hydrogen and oxygen relative to the carbon atoms as well as to each other, results in molecular structures and compounds all of the same total chemical formula but with differing properties; to the chemist they are different compounds.

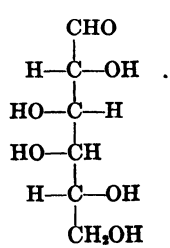
Starch, sometimes known as amylum, is present in some parts of nearly all plants, often in the form of organized or structural granules of varying size. Many starches are known from the names of the plants from which they are derived, such as barley, corn, wheat, arrowroot, rice, potato, and cassava (tapioca). Chemically, the starches are carbohydrates; theoretically their essential structure can be assumed to be built up from glucose, a simple sugar or saccharide. The transformation of starch into glucose, $C_6H_{12}O_6 + H_2O$, was first observed by Kirchoff in 1811. One form of glucose, grape sugar or dextrose, commonly occurs in most sweet fruits and in honey and can be prepared by chemically breaking down more complex carbohydrates, among which might be mentioned sucrose or cane sugar.

Glucose is one of the monosaccharoses. In this same group we find the sugar arabinose, $C_5H_{10}O_5$, whose chemistry was primarily evolved through the study of the hydrolysis of gum arabic. Arabinose may also be derived from tragacanth, ghatti, and other tree exudation gums.

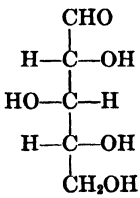
Arabinose contains five carbon atoms and is often referred to as a pentose after the Greek number 5, while glucose with six carbon atoms would be a hexose. Arabinose may be produced from gum arabic, cherry gum, or from beet roots by treatment with dilute acid; *l*-arabinose has the formula:



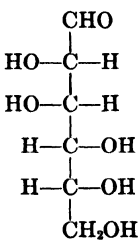
Often associated with arabinose is a hexose sugar galactose, which has the formula



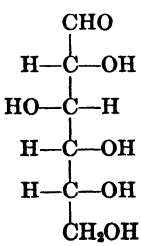
Galactose is found in locust bean as well as in the tree exudation gums, while arabinose and xylose, a pentose, are found together in the seed extracts such as flaxseed, quince, and psyllium. The formula of xylose is given as



Mannose, another hexose, is found with galactose in locust bean, guar, and to a smaller extent in the seaweed extracts. The formula for mannose is



A related sugar, which has the same formula but differs only in spacial arrangement of the carbon, hydrogen, and oxygen atoms, is glucose whose formula is given as



and which is readily produced by hydrolysis of the seaweed extracts as well as by treatment of the hemicellulose of seeds such as psyllium.

The starches are thought of as polysaccharides with the general formula $(C_6H_{10}O_5)_n$ and may represent a storage product of plant life processes to be drawn upon when needed. Starch probably constitutes the source from which the sugar content of plants is derived during the transference of the sap. It is not unexpected, therefore, that gums such as acacia, ghatti, karaya, and tragacanth, which are tree exudations, are complex compounds which on hydrolysis yield various sugars. These sugar-type com-

pounds and their acids and salts may result from the life processes of the plants which convert the starches which the plant has built up into the gum exudations. Lichenin, which is otherwise known as moss starch, is believed by some chemists to be identical with starch amylose, the component of the inner part of starch granules. Starch amylose can be completely hydrolyzed to maltose, which is one of the simple sugars. Lichenin is contained in lichens such as Iceland moss, and the gum extracts from Iceland moss consist of mixtures of cellulose, degraded starches, and simple sugars which, upon hydrolysis, form dextroglucuronic acid. It might be therefore expected that if mankind, with his chemicals, treats starches, gum-like materials could be produced under certain specific conditions. Examples of such products are the dextrins which contain sugars, and the British gums. They might be considered as semi-synthetic products.

The celluloses are the almost universal structural material to impart form and rigidity to plant life. These compounds are also carbohydrates and are closely related chemically to the starches and the sugars. When separated in their pure forms and treated chemically to some extent, the synthetic products thus prepared have gum characteristics.

Table 1 tabulates the various gums and their apparent chemical composition, with some of the products of hydrolysis. Each one of the gums

Table 1. Composition of the Gums

Name	Apparent Chemical Composition	Hydrolysis
Agar	Sulfuric ester of a linear galactan	—
Algin	Polyuronic acid	Cellulose, uronic acid, mannuronic acid
Arabic	Metal salt of complex organic acid	Mixture arabinose, galactose, aldobionic acid, galacturonic acid
British gum	Modified carbohydrate	—
Dextrin	Modified carbohydrate	—
Flaxseed	Heterogeneous polysaccharide	Aldobionic acid, *d*-galacturonic acid, *l*-rhamnose
Ghatti	Calcium salt of polysaccharide acid	*l*-arabinose, barium salt of aldobionic acid
Guar	Complex carbohydrate, galactose, mannose	—
Iceland moss	Cellulose, simple sugars	*d*-glucuronic acid
Irish moss	Calcium salt of sulfuric ester of saccharide	Ethereal sulfates (glucose)
Karaya	Galactan, gelose	—
Locust bean	Carbohydrate, mannose, galactose	Caronbinose (mannose), galactose
Methyl cellulose	Synthetic cellulose ether	—
Psyllium seed	Mixture of polyuronides	Arabinose, *d*-glucose, *d*-xylose, aldobionic acid
Quince seed	Cellulose, arabinose, xylose	Arabinose, mixture of aldobionic acids, cellulose
Tragacanth	Calcium salt of complex organic nature	Glucuronic acid, arabinose

is a complex association of carbohydrates such as celluloses, starches, the sugars, their reaction products, their oxidation materials, the acids and salts in general of compounds whose components are only carbon, hydrogen, and oxygen. The chemistry of the starches is very complex.[32] The chemistry of the sugars is exceedingly intricate and has been the subject of much investigation.[33] A similar situation holds for the celluloses.[34]

Before the middle of the 19th century, living matter was assumed to be composed of a relatively small number of compounds. Brande[35] classified the gums among the "proximate principles of the vegetables."

Newbauer, in 1854, found that the main constituent of commercial gum arabic was an acid substance, which he called arabin or arabic acid. It was said to be composed of carbon, hydrogen, and oxygen, and analysis revealed the presence of the two latter elements in the same proportions as found in water.

In 1868 Scheibler obtained a new sugar by the decomposition of arabin which he called arabinose. The chemistry of the gums remained obscure for many years due to their uncrystallizable properties, which made purification difficult and uncertain.

A method of treating arabin was introduced by Sullivan,[36] in which he found that arabin was composed of an acid nucleus to which a number of mols, consisting of the sugars, galactose, and arabinose, were chemically united. The acid was named arabic acid, and to arabin were assigned the formulae $2C_{10}H_{16}O_8$, $4C_{12}H_{20}O_{10}$, and $C_{23}H_{30}O_{18}$. The names assigned were di-arabinan, tetragalactan, and arabic acid. The formula of arabinose is similar to that of arabin except that the latter contains two additional water molecules ($2H_2O$). The same relationship exists between galactose and galactan.

Baeyer[37] assigned to dextrose the structural formula $CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO$.

Kiliani[38] oxidized dextrose with nitric acid and obtained a monocarboxylic acid, known as gluconic acid. The same number of carbon atoms were found in gluconic acid, $CH_2OH(CHOH)_4COOH$, as in the parent sugar.

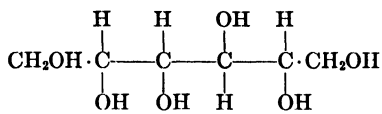
Investigation of some of the other sugars disclosed a resemblance to

[32] Robert P. Walton, "A Comprehensive Survey of Starch Chemistry," Vol. I, 1928, Reinhold Publishing Corp., New York.
[33] Frederick J. Bates and Associates, "Polarimetry, Saccharimetry, and the Sugars," Circular C-440, New York, Bureau of Standards, 1942.
[34] Emil Heuser, "The Chemistry of Cellulose," 1944, John Wiley & Sons, Inc., New York.
[35] W. T. Brande, "Manual of Chemistry," 1848.
[36] C. O. Sullivan, *J. Chem. Soc.*, 1884-1901.
[37] A. Baeyer, *Ber.*, **3**, 63 (1870).
[38] H. Kiliani, *Liebigs Ann. Chem.*, **205**, 182 (1880).

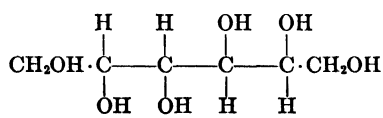
dextrose in that oxidation produced acids containing the same number of carbon atoms. Levulose or *d*-fructose produced acids containing fewer carbon atoms. A modification of levulose is represented by the formula

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot C(=O)\text{—}CH_2OH.$$

Levulose exhibits the reducing characteristics of a carbonyl group, which, on oxidation, breaks the carbon chain to give tartaric and oxalic acids. Reduction of levulose with sodium amalgam yields two hexahydric alcohols, namely sorbitol and mannitol.



(Sorbitol)



(Mannitol)

The reactions of cellulose, reported in small quantities in the algae, fungi, and lichens, resemble those which occur in the simple sugars.

Ott[39] states that cellulose has been identified in *Laminaria digitata*, from which algin and its derivatives are made, by the formation of methyl and acetyl cellulose. Marine algae are said to be similar to cellulose by virtue of the structural material present therein.

Miwa[40] found brown algae contained 5 to 15 per cent cellulose. Brown algae are utilized in the manufacture of the algins.

Glucose, glucuronic, and xylose groups have been isolated from the hemicellulose, and the xylose groups are said to predominate.

Pectin appears to be a polygalacturonide, and is usually associated with arabin and *d*-xylose. Pectins cause fruit juices to "gel."

The uronic acid, associated with the series of *d*-mannuronic acid, has been found in polysaccharide alginic acid.

The celluloses, hemicellulose, and lignins compose the major constituent in a mature cell. This close relationship makes them very similar physically and some of their chemical properties overlap.

Schulze[41] made the first distinction between cellulose and hemicellulose on the basis of solubility in dilute acids.

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[39] Emil Ott, "Cellulose and Cellulose Derivatives," 1943, Interscience Publishers, Inc., New York.

[40] T. Miwa, *Japan. J. Botany* 11 (1), 41 (1940).

[41] E. Schulze, *Ber.*, **24**, 2277 (1891).

Hemicellulose in present-day terminology embraces those cell wall polysaccharides which are extracted by hot or cold alkali and which may be hydrolyzed by boiling with dilute acids to obtain constituents of monosaccharide units. Investigators found that more than one sugar may be formed on hydrolysis and that hexuronic groups may be present.

Various plant mucilages which are water soluble but yield an insoluble residue on hydrolysis have been considered celluloses. Quince seed gum, a hemicellulose, is an example. On hydrolysis it yields an insoluble residue which gives a positive reaction using sulfuric acid and iodine. Its solubility in cuprammonium hydroxide is another indication of the presence of cellulose.

Iceland moss has many of the characteristics of cellulose present in its cell walls. It can be methylated to a trimethyl lichenin which yields 2, 3, 6-trimethyl glucose and a small amount of tetramethyl glucose on hydrolysis.

The differences in the complexities of composition of the various gums as well as in their colloidal behavior account for the differences in their chemical and physical properties. While they are all members of the same general family, each one becomes an individual entity in its application in commerce.

Chapter 2

Gums from the Acacia Tree and Its Varieties

The exudations gathered from the various varieties of acacia trees in many localities of the world constitute an important article of commerce which is often designated *gum arabic,* although also known by a host of other names. The acacia tree has been recognized by mankind for thousands of years and exudations have been collected therefrom since Biblical times. Botanically it is widely distributed in tremendous areas of Africa, stretching from Dakaar and Senegal on the west coast across the continent to the Red Sea throughout Arabia, portions of Persia, India and Australia as well as throughout the rest of the African continent. It is also found in the Western Hemisphere in portions of the lower United States, Mexico, and Central America, particularly in the semi-arid regions, a type of climate which this small thorny tree apparently loves.

The degree of carefulness and the thoroughness of grading, packaging, shipping, and methods of marketing account for differences in various kinds of gum arabic in the commercial sense. In the botanical and chemical sense, too little definite knowledge is available as to the chemical character of the gummy exudations from the different species of the acacia tree. From their commercial uses the most important group of gums are those designated from their origin as Sudan gum, Senegal gum representing the great bulk of the trade, with some minor materials like sunt, suakim, East Indian and wattle gum. Inasmuch as these represent interesting differences in their commercial production and distribution, they are to some extent separately discussed from the viewpoint of gathering them and bringing them into commerce. Chemically they do not differ markedly, their differences being in degrees of color, shade, adhesiveness and viscosity. They are all treated together as gum arabics of different purities.

World production of the exudations from the acacia trees is difficult to estimate, as statistics are not readily obtained and appreciable quantities are employed in local areas or in adjacent districts for native industries. It is estimated that from 30 to 50 million pounds of these exudations enter the stream of international commerce, and that from one-quarter to one-third of this is imported into the United States to serve American industry.

Gum Arabic

Gum arabic application is varied, covering such unrelated uses as adhesives, polishes, confectionery, printing textiles, paper size, inks and pharmaceuticals. Such wide-spread utilization is based upon a combination of unique physical characteristics and their control. As is so frequently the case, industry is ahead of theory, and commercial control in desired limits is usually a matter of rule of thumb.

Among the characteristics of gum arabic are:

1. It is practically completely soluble in water.
2. It is insoluble in most other solvents.
3. Its aqueous solution is highly viscous.
4. Its aqueous solution has a low surface tension.
5. Its aqueous solution is a good emulsifying medium.
6. It behaves as a protective colloid.
7. It does not crystallize.
8. It is usually tasteless or possesses only a slight taste.
9. It is odorless.
10. It is available as a practically colorless to light-brown colored material.
11. It is essentially a metallic salt of a complex organic acid.
12. Its properties may be changed by certain chemical treatments.

Much study has been devoted to these properties but their thorough understanding and control leaves much to be desired. Gum arabic represents a number of commercial materials, plant exudates which vary in physical and chemical behavior in several respects, some in their narrow limits, others over a wide range.

Gum arabic has been known and used since ancient times. Egyptians used it in making paint colors in 2000 B.C. The gum from the Sudan and particularly from Kordofan Province has been an article of commerce since the first century of the Christian era.

Gum arabic in the restricted geographical sense is the material exported chiefly to Europe from Arabia, most of the trade being handled in the port of Aden. Only a very small portion of the commercial gum is collected in Arabia. For several thousand years, natives have gathered the gum from the wild trees in those portions of Africa adjacent to or accessible to the southern end of the Red Sea. In olden times the more important traders who collected from the natives were along the Arabian coast. The gum received its name from them for it was these Arabs who exported the material to Europe. There are indications that caravans carried the gum to North Egypt from Aden as early as the seventeenth

century before Christ. The bulk of the material in earlier times was collected in the areas now known as the Sudan.

In the Middle Ages the trade was largely carried on through Turkish ports or ports under Turkish rule, and the gum was often called Turkey gum, a name still frequently used. There was then a considerable trade in what was called East India gum arabic, chiefly, re-export gums from Africa and Arabia and possibly much Sudan gum which came to Europe by way of Bombay. The trade has developed greatly since the conquest of Sudan by the Anglo-Egyptian forces under Lord Kitchener in 1898 and the subsequent building of the railroad sections so that large areas in the interior are connected with Port Sudan, from whence the gum is shipped to all parts of the world. The gum from French Senegal became an article of commerce long after the Sudan gum was sold.

In a general sense the term *gum arabic* embraces tree exudations of small thorny trees which are varieties or species of the acacia which grow in dry or partly desert places. These trees exist in Central and North Africa, Arabia, and eastward into India as well as in portions of Australia.

There is considerable disagreement among botanists as to the nomenclature and identity of acacia trees particularly in reference to species, subspecies, and varieties. Formerly all the gum arabic was believed to be collected from *Acacia arabica.* There seems to be agreement now that the tree is *Acacia verek* which some botanists consider a variety of Acacia arabica. Other authorities state that the common acacia in the lands from the Red Sea across the African continent to Cape Verde on the Atlantic Coast is the *Acacia verek.* Still others set *Acacia senegal* aside as a separate and distinct species. It is true that the acacias differ in tree size, shape, size of leaf, flower or fruit as do other families of plants. These greater or lesser differences are evident in the acacia trees of Morocco, Senegal, upper Egypt, Arabia and India, but the differences in their exudations are not readily distinguishable in a chemical sense.

In the broad general sense, gum arabic is almost any gum which dissolves completely in water to form a sticky mucilage.

Gum arabic is the dried gummy exudation from stems and branches of the genus *Acacia* which are leguminous trees. A typical "tear" at the point of a man-made tapping is shown in Fig. 2. There are some 400 species in the tropical and sub-tropical regions, chiefly of Africa, parts of Asia and Australia, about 25 of which grow in the Anglo-Egyptian Sudan and the French Senegal sections of Africa. These constitute the most important sources of the gum and are derived from *Acacia verek* or *Senegal.* The best grades come from Kordofan in the Sudan. Gum Senegal refers to the product of West Africa, chiefly French Senegal. The purest grades

of gum arabic are sold under the name "Gum Acacia" and are used chiefly in the pharmaceutical and food industries.

Although it is generally agreed that the origin of gum arabic is due to some process of infection of the tree, there is some question as to whether the infection is bacterial or fungoidal. Acacia trees yield the gum only when in an unhealthy condition. Extreme poorness of the soil with only a trace of salt in it may be the cause in some instances, as evidenced by the good yields where the soil is worn out and unable to produce further crops.

FIGURE 2. Exudation of gum at point of tapping, Kordofan, Sudan, Africa. (*Courtesy The Philadelphia Commercial Museum*)

Lack of moisture in the soil and lack of general atmospheric humidity and other conditions which lessen the vitality of the tree improve the yields. An area defoliated by locusts will put on fresh leaves with its stored sap, and there is no sap left over for production of gum. On the other hand, the vitality of the tree is reduced greatly and in the following season it will be more susceptible to infection and will have a large gum yield. If the rains are heavy the tree will be strengthened and stop the infection and gum production will be smaller. A good seed year is always a poor gum year. Temperature also plays an important role. If after tapping there is a very hot spell the gum exudes well, the greatest exudation coming during the hottest part of the day. A cold spell delays and restricts the yield.

The infection appears to take place through wounds in the tree. Such wounds may be caused by a variety of agencies such as broken branches, grazing camels, beetles that bore into the tree or may be the work of man. To accelerate the process of exudation, the native cuts off the lower limbs of the tree, then nicks the tree with his axe, taking care to cut just under the bark but not into the wood. He lifts the edges of the nick and pulls one up and the other down the tree until they break off. If the weather is hot the tree starts exuding and he collects accumulations, generally weekly until the end of the season. The tapping is done on the trees 3 years of age and older, after the rainy season. Gathering is conducted usually from November to June.

The gum is brought to centers by the native collector, or if he does not own a camel, by a camel owner who buys it from the collector and the gum is auctioned under government supervision. In the Sudan, the merchant who buys it may export it in its natural state, but usually it is graded, cleaned, sifted and bleached before exporting. The best grades are bleached in the sun. When ready for shipment the gum is put in double sacks and sent by rail to Port Sudan for export.

Gum arabic has become generic although it was originally a locality designation, while a number of names are employed indicating the point of origin or the area from which the exudations of the acacia trees originate. These are Sudan gum, Kordofan gum, Khartoum gum, Turkey gum, Sennaar gum, Geddaref gum, Jeddah gum as examples. Although not so broadly used and often employed only locally, similar products are termed Gedda gum, Sennari gum, Turic gum, and Gehzirah gum. In general, the specific varieties of exudations of acacia trees are collected in the Sudan area of Africa, Upper Egypt, Abyssinia or Ethiopia, Somaliland, and adjacent regions or territories.

It is apparent that in the commerce of gum where different grading and preparation methods have become so firmly fixed that they are almost part of the customs of the country, it is inevitable that there appears on the market what looks at first glance like a number of different gums, although chemically they may have considerable similarities and actually belong to the same family. If their physical forms are disregarded, and they be thought of as different grades or different qualities only as a function of varying amounts of impurities resulting from the care or carelessness of the grading, they can then be subjected to bulk processing to convert them into a uniform material of reasonably constant characteristics.

As a background for the understanding of the work of the native collector in various regions, and the activities of the trader, the gathering of Sudan or Kordofan varieties of gum arabic will be described, and later gum Senegal, another regional designation, will also be discussed.

Sudan or Kordofan Gums. Much of this material is marketed through Aden. It constitutes a large share of the gum arabic of commerce and in general it is believed to be the exudation product of *Acacia verek*.

There are extensive forests of acacia in the region of Kordofan which is located west of Khartoum in the portion of Africa now known as Anglo-Egyptian Sudan. The acacia is common in the territory between the Bahrel Abiad or White Nile which is fed from a series of rivers in the southwestern portion of Anglo-Egyptian Sudan, and the Bahrel Adrak or the Blue Nile.

The Blue Nile originates in an area not very far from Addis Ababa, the capital of Ethiopia or Abyssinia. In the central west portion of Anglo-Egyptian Sudan, in the area adjacent to the Sahara, there are large groups of acacia trees in places where there is just sufficient moisture to support vegetation. *Acacia verek* is distinctly a tree of semi-desert regions. Its habitat is peculiar and it requires little of the moisture necessary for other vegetation. It grows naturally in a dry, sandy, barren soil. The trees are small, thorny, and in comparison to American pines, oaks, or beeches, would be considered more shrub-like. In structure to some extent it resembles low-branched young apple trees, although it does not reach the trunk size of the American apple.

In the Sudan area the tree is often called "Hashab" which term the Egyptians and the Arabs also apply to the gum.

There are privately owned forests in which the trees are systematically tapped and the gums collected in an orderly manner with organized groups. This produces the "Hashab geneina" and it is stated that this product is lighter colored than that collected from wild trees. It is probable that the supervision of the tapping, the collection, and grading is better so that a more uniform product results from the privately owned and supervised districts. A gum garden is shown in Fig. 3. There are immense areas in Africa where the acacias flourish. The gum collected from the wild forests is known as "Hashab wady," and because of the multiplicity of individual collectors whose work is necessarily uncoordinated, the wady gum is generally of poorer grade and darker color.

The commercial production of the gum is limited necessarily to those districts not too far from sources of water such as wells or streams. The gum gatherers must carry all of their provisions such as food and water with them, and this limits their collection to areas which are only a few days' journey from depots for replenishment of their water and food supplies. The gum is gathered only in the hottest and driest season of the year, inasmuch as in other seasons the trees flourish normally with sufficient moisture and do not produce gum. The best yields of exuded prod-

ucts result when an unusually hot, dry season follows one which has had a plentiful supply of moisture as a result of excessive rainfall.

Gum collection is not an all-round vocation for the natives but rather is a source of additional income to agriculture at periods when farming is at a standstill. Although the dry season normally begins in the latter part of September or in October and the trees may be tapped any time after the first of November, gum gathering is postponed until the crops are harvested. The gatherers therefore are active only after January or February.

FIGURE 3. Gum garden near Tairara, Kordofan, Sudan, Africa. (*Courtesy The Philadelphia Commercial Museum*)

The men leave their native villages carrying their food and water supply, with a spear for defense against native animals or as a hunting implement. Their only gum-gathering tool is a small hatchet with a long handle, with native woven baskets to serve as containers. A native gum collector may be seen in Fig. 4 with his implements. The gum collector cuts the tree with his hatchet in not too deep a fashion, and then peels a strip of the outer bark an inch or two in width and two to three feet long. Care is taken so that the inner bark is not harmed. The bark stripping operation is not sufficient to harm the tree seriously and in time under favorable circumstances the wound heals. It appears that the gum is formed through

the combination of the process of evaporation of the sap and attack on the plant tissue by a species of bacteria found in or on the bark of the acacia tree. The gum exudes and forms in drops or tears. These tears grow to large size only after a season of good rains which have allowed the trees to become full of sap and develop fresh, vigorous young growth. When first formed the tears are soft, the outside being skin like; but if they are allowed to remain in place for several weeks, the entire mass becomes firm

FIGURE 4. Native gum collector, Kordofan, Sudan, Africa. (*Courtesy The Philadelphia Commercial Museum*)

and hard as a result of evaporation on the surface and diffusion of the aqueous portions from the inside of the tear to the outside. This, however, is slow, as are all diffusion processes.

The gum collectors return with their produce to the villages and sell, barter, or trade their gatherings to local traders or representatives of district gatherers. A gum merchant, with some of his stock, may be seen in Fig. 5. When sufficient stocks are collected, the gum is transported by boat and caravan to the wholesale markets of which Khartoum is typical. Here the gum is picked over, classified and sorted into grades. Grading

is entirely on the basis of superficial appearance and optical judgment, with no chemical control being even remotely thought of. Based on practices of hundreds or even thousands of years' standing, the best grade is reputed to be that of tears which are transparent or almost so, with only a faint departure from a white color, the departure being slightly yellowish or straw. The gum is spread in the sun and in thin layers to bleach. The best area, according to the natives, to perform this is on the low sandy

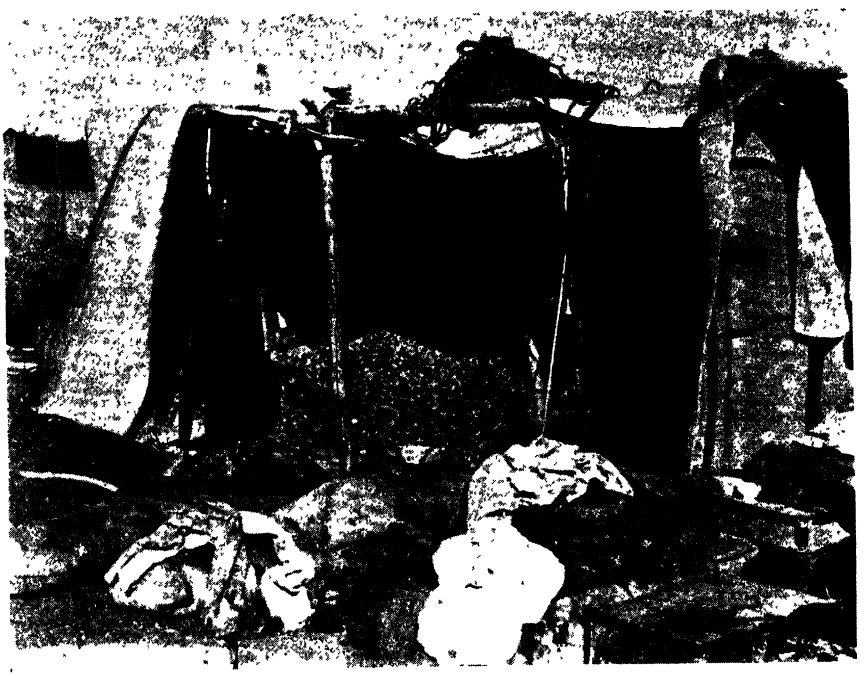

FIGURE 5. Gum merchant, Tairara, Kordofan, Sudan, Africa. (*Courtesy The Philadelphia Commercial Museum*)

shore of the Nile River. Gum picking and sorting, after bleaching in the sun, are shown in Fig. 6. The drying out in the sun is at a rate faster than the moisture can diffuse from the inside of the tears, so that with expansion and contraction after drying, the tears are filled with innumerable minute cracks. These cause the gum to assume an opaque appearance and a greater degree of whiteness. It is therefore typical of the commercial varieties of good grades of gum arabic. It is unfortunate, however, that this optical appearance does not carry with it any indication of the factors of its use such as color of solution, viscosity, clarity, and freedom from insolubles. The trade grades which are cheaper are yellowish to red in color,

while the poorest may show an appreciable amount of impurities, these being dirt, bark, and sand which often are very finely distributed through the mass of the gum.

The gum from Kordofan, Sudan, the White and Blue Nile areas is often referred to as Sudan gum. The common commercial grading is on the basis of the color and size of the gum drops, particles, or tears, or portions thereof referred to as fragments. These gradings are "bold," which means cleaned, bright, and the largest of the particles; "large," which is a grade just below "bold;" "medium," referring to a relatively smaller size without necessarily the bright appearance of the "bold" pieces; "granular," referring to secondary fragmentary pieces; "pickings," having reference to

FIGURE 6. Gum picking, Omdurman, Kordofan, Sudan, Africa. (*Courtesy The Philadelphia Commercial Museum*)

material which is sorted out and not of the same quality as the previous grades, being smaller in particle size, darker in color, and with greater amounts of impurities; and "siftings," which are the residue of the operations and would correspond in a sense to a dust grade in the resinous trade. The siftings have value for their gum content, but on the basis of their optical appearance they are definitely secondary products. The designation of "sorts" refers to a grade which has not been picked and classified into different grades, but is really a random collection of all of them. Sooner or later, however, the sorts become classified into different groupings, and instead of being a random collection attempt to match certain optical properties of grades previously supplied.

The traders and the shippers as well as the merchants often talk of "hard" gums to indicate that the gum is not brittle. This hard gum is composed of the larger solid, glassy particles or tears. It has been held in

the past, when there was much less science in the applications of the gums, that this hard gum was a stronger adhesive material and gave a higher viscosity as compared to the softer gums. There seems to be no direct relationship between these properties, inasmuch as it is only a general rule which has a considerable number of exceptions. It may be that there are some structural and minor chemical differences between the hard or strong gums, inasmuch as these are produced from the young, weak trees. The softer gums ordinarily are produced by the trees in more vigorous health and with fewer injuries. The bleaching characteristics of the hard glassy gums differ from those designated as soft, in that the softer ones bleach more readily. As a result, the hard gums are more likely to show traces or remainders of yellow or reddish colors.

The native sorts, or gum "as it comes," may be further classified by wholesalers, as those formerly operating in Trieste who marketed the hard gum under the name of Khartoum gum and designated the softer material as Kordofan gum.

Gum Senegal. Gum Senegal is reputed to be not quite as clean as the Kordofan grade of gum arabic and is less preferred by the American importers and their customers. It, however, finds a large European market. Unless it be subjected to further mechanical and chemical processing, the gum Senegal grades are generally believed to be not as adhesive as those of the Kordofan gum but form solutions of greater viscosity.

Gum Senegal is also known as Berbera gum, gomme de Galam, gomme de Podor, gomme de Tombouctou as well as a number of other local names. The gum is gathered from forests of small thorny trees which cover great areas in the regions west and southwest of the Sahara and the French Sudan, through Senegal, Gambia, the French Sudan, the Ivory Coast, northern Dahomey and Nigeria. The acacia trees here have not been clearly defined nor designated by the botanists, and embrace *Acacia Senegal, Acacia claucophylla, Acacia abyssinica, Acacia albida,* and *Acacia verek.* The forest areas are dry and barren during a great part of the year. A large portion of the material reaching the market is from the country north of the Senegal River, a region which is easiest for the natives to penetrate, and which is close enough to the coast and the routes of the traders. In the region of the greatest gum collections, abundant rains occur from July to November. The rainfall is so heavy that large areas become temporary swamp land. During these periods the trees grow luxuriously and become filled with sap with abundant new growth. The rainy season ends abruptly being followed by a period of hot, dry, scorching, high velocity east winds. The rapid change in weather shrivels the trees so that the outer bark soon dries and cracks with the formation of many open fissures and sources of infection for gum formation.

Within a few weeks from the onset of the dry season the trees produce gum exudations in considerable amounts. The lighter colored (gomme blanche) is that collected in the early part of the season, in January and February, while the slightly darker shade, the gomme blonde, is that gathered in March or April.

As is the case with other agricultural products from wild forests in tropical regions, the work is limited to areas not too far from sources of water, food, and supplies. For many years the gum trading and the export business were very methodically handled by French organizations at St. Louis and Rufisque, in French Senegal on the west coast of Africa. The traders have strict procedures for the gathering of the gums and dealing with the natives, as well as the barter and trade and appointed times at which the expeditions go up the river to the native collecting centers. Deliveries to the port areas are by river boats and camel caravans. Much of the material is exported to France in normal times, particularly to Bordeaux. During World War II there was considerable interruption, and when relief of the shipping shortage was evident quantities of the material came to the Western Hemisphere.

The French classification on a commercial basis was (1) "Gomme du bas du fleuve," or "Gomme de Podor," from lower Senegal; (2) "Gomme du haut de fleuve" or "Gomme de Galam," from upper Senegal; and (3) "Gomme friable" or "Salabreida," respective designations for lower grades. In general the gomme du bas du fleuve was the highest quality. Sorting is done into whole and broken tears and then the whole tears separated into commercial grades according to "bold," "large," and "medium" designations as well as the lower siftings and screenings. In a manner similar to that employed for Sudan gum, the highest qualities are the largest, palest, and hardest of the tear shapes.

The white gum or "gomme blanche" is subdivided on a size basis into the "surblanche" or bold, the "grosse blanche" or large, the "petite blanche" or small, and the "premiere blanche" and "seconde blanche."

The yellow grades or "gomme blonde" become the large or grosse blonde, the small or petite blonde, the "blonde larmeuse" and the premiere and seconde blonde. In Gum Sengal, the worm-like or vermicelli forms are separated and marketed as a separate grade. There are in addition some special classes of large tears of an inch and a half or more in diameter termed "boules" and further subdivided in terms of size into "grosse" and "petite" and in terms of color into "blanche" or white, and "blonde" or yellow, as well as "rouge" or red, or "lavees." Broken sections of tears are classified into an industrial grade termed "gomme fabrique" and are further subdivided into "grosse" or large, and "petite" or small. Some botanists are of the opinion that the gomme fabrique, which seems to be

a more friable gum and is in irregularly shaped pieces, is a product of *Acacia adscendens,* or *Acacia adansonia,* while still others are of the opinion that the gum is a product of *Acacia albida.* Still other authorities are of the opinion that the *Acacia albida* is responsible for the "gomme friable" or "salabreida." This material is relatively brittle, and is usually in small fragments and is nearly white in color.

There are some qualities of very impure gums. There is one grade which contains much dirt and particles of bark. This is often loosely-textured irregular lumps a couple of inches in diameter and appears to be somewhat matted together. It is often designated as "Marrons et bois."

In general, Senegal gum is yellower or redder than the relatively pale gum from the eastern Sudan and particularly from the cultivated or restricted Geneina area of Anglo-Egyptian Sudan. The tears of Senegal gum are usually larger in size than those of Sudan gum and are less brittle. There is therefore ordinarily a smaller quantity of fragments, or of broken-down gum pieces, or of gum dust. Senegal gum does not crack as easily as the sun-bleached Sudan gum, and in general there is little of it which appears to be white and opaque. These optical differences are relied upon to distinguish Senegal varieties of gum arabic from the Sudan varieties of the same material.

Sunt Gum. There appears to be agreement that small amounts of gum are gathered in the Sudan and adjacent territories from the tree *Acacia arabica.* It is probable that gum from this tree, particularly gathered from the forest areas, is unconsciously mixed with the gum from other acacia trees. That specifically collected from the *Acacia arabica* is often sold under the name of Sunt. It is stated to be inferior to the Sudan gum from *Acacia verek,* it being considerably weaker and more brittle. The form in which it generally reaches the market is that of broken fragments of white or pale yellowish color. The native gatherers bruise the tree around a cut which they have made in the bark, two to three inches in diameter, in order to stimulate the secretion and formation of the gum. In the American market, Sunt does not appear to be important except as it occurs in mixtures.

Suakim Gum. This variety of gum arabic or gum acacia appears to be the production from several species or varieties such as *Acacia verek, Acacia seyal* variation *fistula, Acacia stenocarpa,* and *Acacia procera* among others. It is from the areas and regions adjacent to the western shore of the Red Sea, although some of the material may be brought by caravans from distant points. As a result of its relatively unsupervised collection, it is ordinarily of inferior quality although the quantities are important. It is often brittle and reaches the market as a coarse powder similar to Talh gum. This material in two varieties, the red and the white,

is gathered from *Acacia seyal* which is found widely distributed in the Sudan. It is sometimes referred to as talca or talba gum by the natives. The gums from *Acacia gerugera* and *Acacia suma* are similar in quality and are also distributed in their habitat in the Sudan.

Some gum is gathered in the northern part of Africa but it is probable that considerable of the material which reaches there has been brought by caravans from the south of the desert. It is known that gums are gathered from *Acacia arabica, Acacia verek,* and *Acacia nilotica* in miscellaneous manners and gathered, rather than by organized caravans, by what might be termed "tramp" traders who transport gums as portions of a miscellaneous cargo. From their point of entrance into commerce such as the Barbary State, Morocco or Mogador, they are often designated by the names of Barbary gum, Morocco gum, and Mogador gum.

Miscellaneous Locality Gums Derived from the Various Species of Acacia. The term East Indian Gum from India is a misleading one and at the outset must be distinguished from those resinous materials which are designated in the trade as Pale East India or hiroe or rasak.[1] When referring specifically to gums of the water-soluble or water-dispersible varieties, the term is still very indefinite and includes gums from many districts and several species, such as *Acacia stenocarpa, Acacia arabica, Acacia fistula, Acacia verek, Acacia leucophloea, Acacia modesta, Acacia odoratissima, Acacia farnesiana, Acacia lenticularis, Acacia ferruginea* as well as others. There appears to be random collection and transportation of these materials and a large percentage comes to Bombay from Red Sea ports on the African coast. Some of it, however, is collected in various parts of India and finds its way to the trading and exporting centers.

A particularly specific Indian gum is that designated as Babool which shows in a number of cases complete dispersion or "solubility" in cold water. In general, however, because of their random collection and sorting, the East Indian gums are of inferior quality and also they may be mixed with other gums such as those of ghatti. Ghatti is discussed separately in this volume in Chapter III.

The *Acacia catechu* tree, which yields catechu extract or cutch, produces a gum which is yellow to dark amber in color, in tears which are sometimes as large as an inch in diameter. The gum has a sweetish taste, is ordinarily completely soluble, and forms a strong mucilage with cold water. The product is much used in India and often in textile applications as a substitute for the normal gum arabic. Some of the exudations of the tree reach the normal commercial markets, but largely as an admixture in the East Indian gum.

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[1] C. L. Mantell, C. W. Kopf, J. L. Curtis, and E. M. Rogers, "The Technology of Natural Resins," John Wiley & Sons, Inc., New York, 1942.

Wattle Gum. This material is gathered in Australia from several species of acacia, specifically *Acacia pycnantha,* or the tree known locally as the black wattle gum tree, *Acacia decurrens,* the silver wattle gum tree, *Acacia dealbata, Acacia sentis* and *Acacia homalophylla.* The gum is usually hard, glassy and in most cases fairly transparent. It is much darker in color than the true gum arabics, being dark reddish, and with cold water forms a strong mucilage although some samples are not completely soluble in cold water. The gum is distinctly different from the gum arabic in that it has a strongly astringent taste and has an analyzable quantity of tannin derived from the bark.

It would appear that the gum production is secondary to the utilization of the trees for wattle bark employed by the tanners in the conversion of hides to leather.

It is to be remembered that large areas of Australia are arid and desert-like in character. The wattle trees which exist in the very dry regions, particularly west of the mountains in South Australia and in New South Wales, are the sources of the best qualities of wattle gums. Apparently gathering is not organized nor is tapping practice systematic and regular. Other industries compete for the services of those who might be engaged in gum gathering, so that the commercial supply is irregular and at times scanty.

Although there are many gradations of wattle gum, in general these gums of Australia and South Africa are of two types. The first is almost entirely soluble in water while the second leaves more or less swollen but insoluble gums. In his account of the wattle gums, J. H. Maiden[2] classified the soluble gums as coming from *Acacia farnesiana, Acacia ferruginea, Acacia leucophloea,* while the so-called insoluble gums are collected from *Acacia decurrens, Acacia mollissima,* and *Acacia vestita.* A number of the wattle gums are low in mineral content, showing values of 1 per cent or less, and they are all low in viscosity in their water solution or dispersion. The wattle gums are distinguished from the gum arabic, in that they have a much greater proportion of galactan and a smaller amount of araban. In general, these gums are very plentiful and exude largely and freely in tears of good size and in large masses. The viscosity, however, is low, and this restricts the demand for them in comparison to other gums.

Cape gum from Cape Colony in the Union of South Africa is somewhat similar to Australian wattle gum in appearance and quality. The cape gum is from a large, very thorny native tree, *Acacia horrida* and *Acacia giraffae.* In contrast to the desert acacias, these trees grow to thirty to forty feet in height and have trunks of the order of a foot or two in diameter. Locally the trees are often used for hedges. At times in the

[2] J. H. Maiden, *Pharm. J.,* **20,** 869-980 (Apr. 26, 1890).

past the gum has entered commerce in appreciable quantities and there appears to be possibility of a fairly large production were the business of gathering organized systematically. Other demands for labor, and usually more profitable ones, cause local lack of interest.

In the Western Hemisphere trees of the acacia family grow in dry or desert regions and periodically samples of gums from the southwestern portion of the United States or from Mexico appear on the market. Samples of gum occasionally are collected in Central and South America from various varieties of acacia, particularly *Acacia farnesiana.* Ordinarily they are dark in color, being yellow to red, and with the exception of small local production the average quality is poor. They present the problem of lack of continuity in terms of supply. Many of them find local usage and do not enter the international trade streams.

Grading by American importers is based upon (1) the source of the gum arabic, that is from which types of acacia trees and the area in which it is collected and sorted, (2) color and (3) size. Such grading is not entirely satisfactory and the different shipments of the same grades vary in color, flavor, viscosity and other respects within rather wide limits. Kordofan gum (hashab geneina) which designates the gum from *Acacia verek* from private cultivated gardens in Kordofan Province in the Anglo-Egyptian Sudan is considered the best type. There are a number of grades of Kordofan; the grade which is cleanest, whitest (sun bleached) and without taste is called gum acacia and is used in food preparations and pharmaceuticals. Of the many other grade designations of Kordofan there are included:—

Kordofan cleaned
Kordofan cleaned and sifted
Kordofan bleached extra fine
Kordofan bleached No. 1
Kordofan bleached No. 2

The American market uses Kordofan gum principally. Gum Senegal is not as clean as the Kordofan grades and finds a limited use in this country. It is used extensively, however, in France and Germany.

There are many trade designations, some indicating the port from which it is shipped or the numerous names that dealers apply to their products, including also "U.S.P." and "Technical."

Gum arabic appears on the market as irregular tears of various sizes or as a transparent amorphous powder, the color varying from white to yellowish-brown and even darker. Color influences price greatly, the highest price being commanded by practically colorless material. Poorer grades may be pale rose, darker pink or yellowish.

There appears to be a close relationship between color and flavor.

Deeply colored samples generally have an unpleasant taste. The color is due to the presence of tannins which have an astringent taste. At least part of the color in inferior grades is due to tannins contained in the bark-contaminated product, but even gums free from bark are often colored. Opinions differ as to the origin of the tannin in the latter. Some hold that it is derived from bark in contact with the exudation, others that it is formed in the gum by chemical changes.

It is often difficult to predict the color of the gum arabic solutions on the basis of the color of the dry tears or powder. The size and condition of the lumps and powder affect judgment considerably. The smaller the size and the more frosted, the lighter will their color appear, and a dark gum when finely powdered appears to lose its color. The color of a transparent substance like gum arabic is revealed by light passing through a considerable thickness of the pieces. When the gum is finely powdered or its surface is crazed, it presents so many minute facets at all angles that practically all the light is reflected and scattered before it has traversed more than the outermost layers of the substance. Proper comparison of color should be made in solutions of a definite concentration. According to Hamy[3] the rotatory power of solutions of gum from *Acacia verek* is negative, that from other species of acacia is positive.

Gum arabic contains both oxidases and peroxidases which may be inactivated by heating a gum solution at 80°C. or higher for 1 hour.

The specific gravity of commercial samples of gum arabic is generally 1.35 to 1.49 but samples dried at 100°C. are higher. Moisture content usually is between 13 to 15 per cent. A gum with a moisture content of more than 15 per cent is difficult to crush and sift and samples with less than 12 per cent are friable and likely to dust and chip badly. Ash content varies from less than 1 per cent to several per cent in samples containing sand and other dirt. In clean samples magnesium and potassium with smaller amounts of iron and manganese are present also. Although highly soluble in water the gum frequently contains insoluble portions. Gum acacia will generally have less than 1 per cent water-insolubles.

The earliest exudate does not form a limpid solution, yielding on the contrary a mucus-like fluid. After two or three months' storage a change takes place, probably due to the enzymes, so it dissolves entirely.

The aqueous solution is clear and acid in reaction, the degree of acidity varying widely in different samples. Mason[4] quotes the work of two investigators who reported 0.002 and 0.011 gram potassium hydroxide respectively as required to neutralize 1 g. of gum.

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[3] A. Hamy, *Bull. sci. pharmacol.*, **35**, 421-2 (1928).
[4] C. F. Mason, *Chem. Ind.*, **53**, 680 (1943).

The high solubility of gum arabic in water is demonstrated by the solubility measurements of Taft and Malm.[5]

Temperature °C.	% Solubility
25	37
50	38
90	40

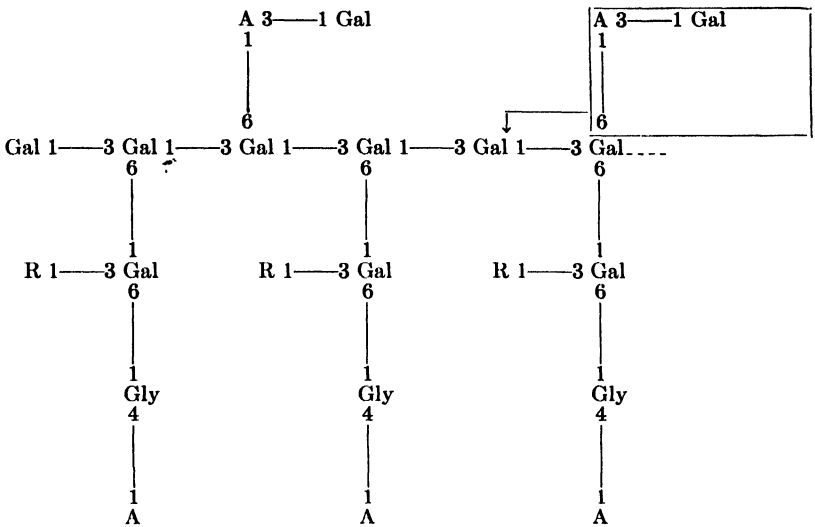
Taft and Malm[6] also studied the solubility of gum arabic in an extended list of organic solvents including aliphatic and aromatic compounds, alcohols, ketones, ethers, esters, halogen derivatives, glycols, pyridine, hydrocarbons, and others and also liquid ammonia, but none were effective as solvents except ethylene glycol and glycerine which were effective but slowly. By heating to 75°C. over a period of several days and thus reducing the viscosity, quite appreciable amounts dissolved. In the case of ethylene glycol 1.4 grams of gum dissolved in 25 cc. (approximately a 4.8 per cent solution) and remained in solution after cooling. Very slight solubility at 75° was rated with acetates and mixtures of acetates with alcohols. The insolubility of gum arabic and arabic acid in aqueous alcohol solutions of more than 60 per cent alcohol makes possible the preparation of the gum (arabic) acid.

The following reagents in solution give precipitates or heavy jellies on addition to gum arabic solutions:—borax, ferric chloride (excess redissolved), basic lead acetate (but not neutral lead acetate), potassium and sodium silicates, gelatin, Millon's reagent[7] and Stokes acid mercuric nitrate reagent.[7] Dilute acids hydrolyze gum arabic yielding a mixture of arabinose, galactose, aldobionic acid and galacturonic acid. Treatment with nitric acid yields mucic, saccharic and oxalic acids.

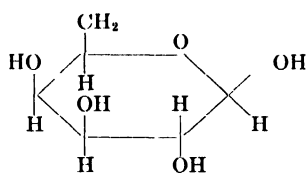
A great deal of research has been carried out on gum arabic revealing many points of interest as to its molecular structure and its physicochemical behavior. As is so often the case, industrial utilization has been far ahead of the purely chemical understanding, but the newly acquired theoretical understanding should unfold new opportunities for wider and more intelligent utilization.

In structural complexity the gum arabic "molecule" stands between hemicellulose and the simple sugars. Actually, gum arabic of commerce is a mixture of gums dried and stored under conditions which do not always give the same chemical entities. It is not a substance of empirical composition. Essentially it is a mixture of calcium, magnesium and potassium salts of arabic which Hirst[8] pictures as: 1*d*-glycuronic acid, 3*d*-galactose, 2*l*-arabinose, 1*l*-rhamnose, arranged as in Fig. 7.

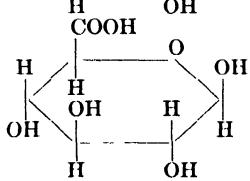
[5] R. Taft and L. Malm, *Trans. Kans. Acad. Sci.*, **32**, 49-50 (1929).
[6] R. Taft and L. Malm, *Trans. Kans. Acad. Sci.*, **34**, 116-117 (1931).
[7] See Chapter 15, Specifications, Identification and Testing.
[8] E. L. Hirst, *J. Chem. Soc.*, 70-8 (Feb. 1942).



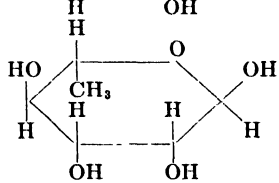
Gal = *d*— Galactopyranose



Gly = *d*—Glycuronic acid



R = *l*—Rhamnopyranose



A = *l*—Arabofuranose

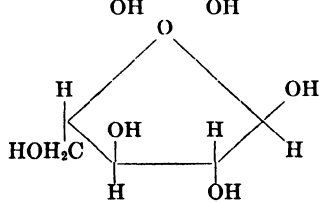


Fig. 7. Gum arabic "molecule"

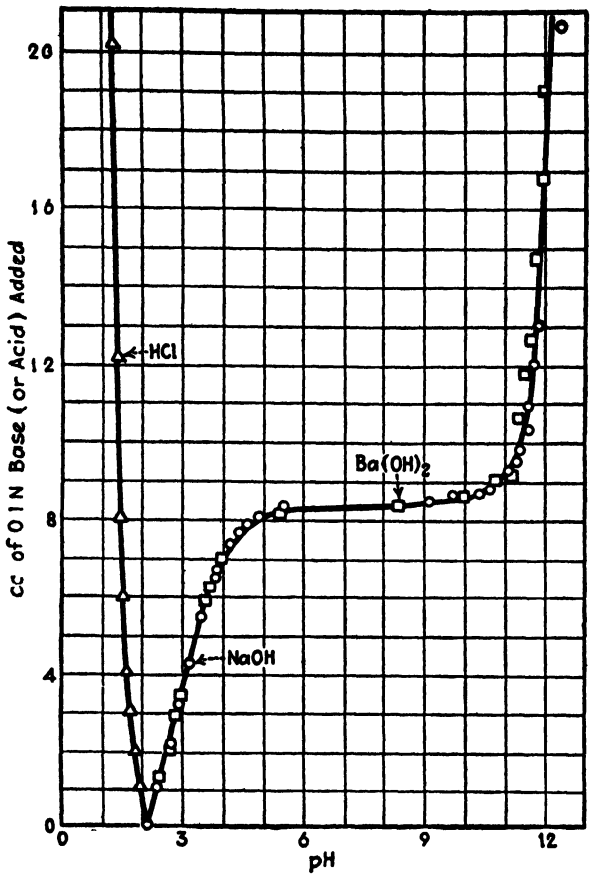
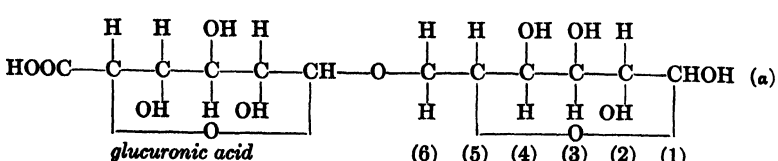


FIGURE 8. Titration of arabic acid with acid and alkali.

Research workers have hydrolyzed gum arabic and obtained the various constituents and a crystalline aldobionic acid has been isolated,[9] experiments indicating it to be α (or β) glucurono-3 (or 6) α-galactose, the α-6 compound probably being represented by:



Aldobionic Acid (1 glucurono—6 galactose)

[9] M. Heidelberger and F. E. Kendall, *J. Biol. Chem.*, 84, 639-53 (1929).

Oakley[10] demonstrated the molecular weight of gum arabic to be of the order of 240,000 and various workers[11] have shown that the equivalent weight of the gum acid is of the order of 1000 to 1200.

The gum acid may be freed from its mineral content by precipitating the acidified aqueous solution of gum arabic with alcohol (the gum is insoluble in solutions containing more than 60 per cent alcohol), redissolving in water and reprecipitating several times until ash free. Prolonged contact with alcohol, however, changes the gum to a water-insoluble product and accordingly a second method is generally found superior. This method electrodialyzes the product obtained after two or three alcohol precipitations of the acidified aqueous gum arabic.

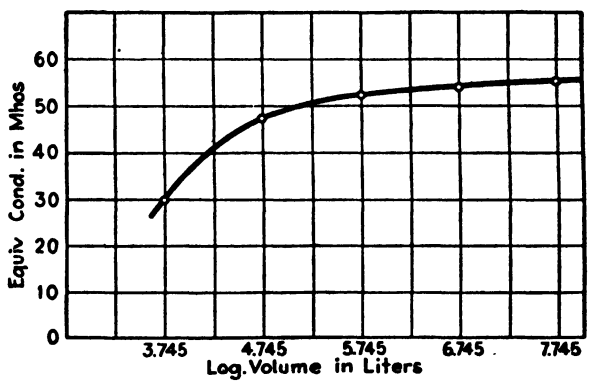


FIGURE 9. Conductivities of gum arabic solutions.

For a material which exhibits so many typical colloidal properties, gum arabic and its gum acid exhibit several unexpected physicochemical characteristics.

Despite its high molecular weight and high equivalent weight the gum has a strong acid titration curve[12] as shown in the graph in Fig. 8. The pH value of a 1 per cent solution of the pure "gum acid" was 2.7 which is the same as that of a 0.002 *N* solution of hydrochloric acid. Taft and Malm[13] conclude from a study of the behavior of gum arabic that it is a strong electrolyte, the calcium and magnesium salt of a complex acid. Their results of freezing point and conductivity as functions of concentration are shown in Fig. 9.

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[10] H. B. Oakley, *Trans. Faraday Soc.*, **31**, 136 (1935).

[11] A. W. Thomas and H. A. Murray, Jr., *J. Phys. Chem.*, **32**, 676-97 (1928) and others.

[12] A. W. Thomas and H. A. Murray, Jr., *loc. cit.*; see also L. Amy, *Bull. soc. chim. biol.*, **10**, 1079-90 (1928); R. Taft and L. Malm, *J. Phys. Chem.*, **35**, 874-92 (1931).

[13] R. Taft and L. Malm, *J. Phys. Chem.*, **35**, 874 (1931).

Nord[14] and Nord and von Ranke-Abonyi[15] found that when gum arabic solutions are frozen one or more times, there is an increase in the surface tension, speed of cataphoretic mobility and electrical conductivity, the latter for solutions above 0.1 per cent; solutions of 0.01 per cent concentration show a decrease both in electrical conductivity and in viscosity.

The relation of concentration and freezing point of gum arabic solutions is shown in Table 2.

Table 2. Relation Between Concentration of Water Solution of Gum Arabic and Freezing Point

No.	Percent by Weight	Freezing Point (°C)
1	4.38	0.100
2	5.83	0.136
3	6.51	0.148
4	7.55	0.165
5	8.41	0.198
6	12.45	0.356
7	14.52	0.430
8	15.13	0.456
9	17.55	0.563
10	24.50	0.850
11	27.50	1.100
12	29.00	1.200
13	30.00	1.400
14	32.50	1.600
15	35.00	1.800
16	36.00	2.000
17	37.50	2.200
18	38.50	2.400
19	41.20	2.700
20	42.80	3.000
21	43.80	3.200
22	44.80	3.400
23	45.90	3.600
24	46.90	3.700

The viscosity of gum arabic solutions is affected by a number of factors some of which are beyond human control. Viscosity of one shipment of the gum may be as much as 50 per cent greater than that of another of apparently the same grade. Age of tree, the effect of rainfall, early exudation as contrasted with later exudation, storage conditions, pH, addition of salts, temperature and type of viscosimeter seem to play a part. If in dissolving the gum the whole of the water necessary is added at the outset, a somewhat higher viscosity may be obtained than

[14] F. F. Nord, *J. Indian Chem. Soc. Prafulla Chandra Ray Commemoration Vol.*, 251-83 (1933).

[15] F. F. Nord and O. M. von Ranke-Abonyi, *Science*, **75**, 54-5 (1932).

if only part is added at first and the solution later diluted to contain the same amount of water.

It is advisable to allow solutions to stand undisturbed for a few hours before testing the viscosity. Dr. Beam at the Gordon College, Khartoum, found that a solution made by adding water to powdered gum and left overnight, then agitated until apparently homogeneous and filtered, continued to diminish in viscosity for about an hour after filtration. The final viscosity was 10 per cent lower than that right after filtering.

The viscosity behavior of gum arabic solutions is one of its most important characteristics. Although low concentrations of gum in water yield viscous solutions, the high solubility of the gum permits solutions with very high viscosity. High viscosity of the gum is important, for example, in making and stabilizing emulsions and suspensions. Its retention of high viscosity over wide ranges of pH and in mixtures with other emulsifying agents permits flexibility of properties. It may be mixed with tragacanth and agar-agar for stabilizing emulsions; it may not be used, however, with soap in making emulsions. Its incompatibility with soap is at least partly due to its calcium and magnesium content.

Gabel[16] reports that heating specimens of acacia or drying them over sulfuric acid increased the viscosity of their solutions. The average viscosity of the unheated or undried control was 12; heating to 40°C. for 48 hours increased the viscosity to 14.5; heating at 100° for 72 hours resulted in a viscosity of 61.4.

Supersonic waves decrease the viscosity of gum arabic solutions.[17]

Taft and Malm showed the effect of concentration of the gum on viscosity and density. The rise in viscosity is accelerated greatly as the concentration goes above 25 per cent, though the density increase is directly proportional to the concentration as shown in Table 3. The relative viscosity in the table furnishes a comparison with that of water, considered as 1.00.

Temperature affects the viscosity of gum arabic solutions and the density of the solutions as well, as illustrated in Table 4 by Taft and Malm. The viscosity of gum arabic as well as of the gum acid is lowered by addition of salts.

Tendeloo[18] found that addition of electrolytes decreases the viscosity of 1 per cent gum arabic sols. If a single electrolyte is added the viscosity decreases as the valence of the anion increases or as the concentration of the electrolyte increases. The effect of equivalent concentrations of mixed electrolytes is additive. The influence seems proportional to the total

[16] L. F. Gabel, *J. Am. Pharm. Assoc.*, **19**, 828 (1930).
[17] *J. Chem. Soc.*, Japan **56**, 843 (1935).
[18] H. J. C. Tendeloo, *Rec. trav. chim.*, **48**, 23 (1929).

amount of electrolytes present. Tendeloo postulates that the influence of the electrolytes is of a capillary-electric character; ions alter the electric charge of the micelles which corresponds to a diminution of the

Table 3. Relation of Concentration of Water Solution of Gum Arabic to Density and Viscosity

Percent Gum by Weight	Density g./cc.	Absolute Viscosity	Relative Viscosity
1.22	1.000	0.0132	1.65
2.10	1.003	0.0160	2.00
2.70	1.006	0.0184	2.30
3.85	1.010	0.0234	2.92
3.95	1.011	0.0235	2.93
4.77	1.014	0.0259	3.23
5.54	1.017	0.0287	3.59
7.33	1.024	0.0390	4.87
8.55	1.029	0.0440	5.50
11.73	1.042	0.0707	8.84
15.68	1.050	0.0959	11.90
16.48	1.062	0.1400	17.50
18.69	1.071	0.190	23.70
34.92	1.141	2.410	300.00

Table 4. Effect of Temperature on Specific Gravity and Viscosity of 9.09% Gum Arabic Solutions

Temp. (°C.)	Density (g/cc)	Relative Viscosity
0	1.197	7.17
15	1.034	6.57
30	1.031	5.97
45	1.025	5.48

degree of hydration, and the magnitude of the effect depends upon the valence of the ions adsorbed.

Viscosity of the gum acid changes markedly with pH, the maximum being in the range of neutrality. This is shown by Fig. 10. Addition of salt also lowers the viscosity.

Briggs[19] studied the osmotic pressure of arabic acid and sodium arabate derived from gum arabic.

Electrodialyzed arabic acid was neutralized with sodium hydroxide and dried in vacuo. The salt contained 85×10^{-5} equivalent of sodium per g. This salt and varying proportions of sodium chloride and hydrochloric acid were dissolved together. Equal amounts of a sample were placed in each of two collodion sacs. To one sac was added 10 cc. of distilled water. The two sacs were then suspended in pure water and subjected to the

[19] D. R. Briggs, *J. Phys. Chem.*, **38**, 1145-60, 867-81 (1934).

same uniform pressure of such intensity that equilibrium would be reached by passage of water from one sac and entrance into the other. When the volumes in the two sacs were equal, equilibrium had been reached. The pressure was maintained by blowing air into a tube connected to the upper part of the sacs and vented by a tube which projected into a vessel of water. The depth of the projection determined the pressure. The data show: (1) Equilibrium is independent of pore

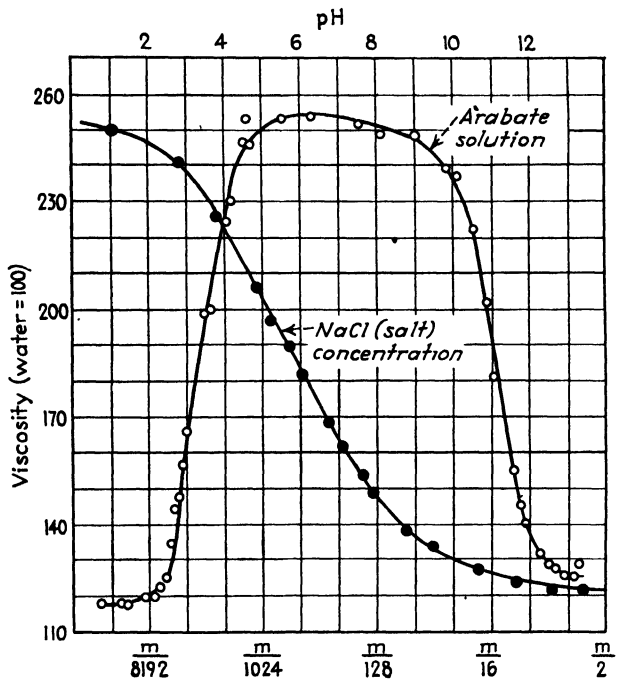


FIGURE 10. Viscosity of arabate solution as affected by pH and salt concentration.

size or kind of membrane; (2) the equilibrium among diffusible ions is in accord with Donnan's theory; (3) the calculated osmotic pressure, P_c, exceeds the observed osmotic pressure, P_o, by a value P_x such that

$$\frac{E\alpha'[k]_i^{0.211}}{P_x} = \text{constant},$$

where E is the potential across the membrane, α' is a measure of the number of equivalents of small diffusible ions derived from 1 g. of colloid, and $[k]_i$ is a measure of the concentration of salt inside the membrane other than the colloid. A diffusible nonelectrolyte, ethyl alcohol, up to 0.5 molar had no effect on this relation.

Glarum[20] measured in a Stormer viscosimeter the fluidity of castor oil, various gums and starches and a textile printing paste. The fluidity in terms of revolutions per second divided by the load for the castor oil and gum arabic remained fairly constant over a wide range in load, as would occur with true solutions, but the other solutions tested showed increasing fluidity with greater loads. In the case of gum tragacanth the fluidity increased 54 times for a load increase of 6 times. A solution showing such behavior gives a shorter and more false body than one containing gum arabic.

Structural viscosity is the term applied to solutions whose rate of flow in capillaries is not proportional to the pressure, the viscosity decreasing with increase of pressure. Several workers have reported that gum arabic solutions do not show structural viscosity, e.g., Coumou[21] for 20 per cent gum arabic solution. Ostwald,[22] on the other hand, showed structural viscosity occurs in gum arabic sols at high concentrations (up to 45 per cent) if the temperature is kept low enough such as at 20°C., and at pressures below 10 cm. water.

Rowson[23] found that the addition of a solution of gum acacia in any proportion to a solution of gum tragacanth results in a dehydration of the gel masses of tragacanth and their deposition as white floccules, the viscosity of the mixture being lower than that of either constituent solution. A minimum viscosity was attained in a mixture consisting of 80 per cent tragacanth and 20 per cent acacia despite the fact that the viscosity of the acacia solution was one one hundredth that of the tragacanth mucilage. Starch and sucrose solutions did not have a similar effect on tragacanth solutions.

COAZERVATION

Bungengerg de Jong and co-workers in an extensive series of studies have investigated coazervation,[24] a term they have proposed for the separation of lyophilic colloids into two liquid phases; coazervate being the term applied to the heavier, colloid-rich layer. When a solution of gum arabic, which has a negative charge at all pH values, is mixed with a solution of gelatin at pH below its isoelectric point, separation of a

[20] S. N. Glarum, *Am. Dyestuff Reptr.*, **26**, 124 (1937).
[21] J. Coumou, *Chem. Weekblad.*, **32**, 426 (1935).
[22] W. Ostwald, et al, *Kolloid-Z.*, **67**, 211 (1934).
[23] J. M. Rowson, *Quart. J. Pharm.*, **10**, 404 (1937).
[24] *Biochem.-Z.*, **213**, 318 (1929), **221**, 182, 392, 403 (1930), **232**, 338 (1931), **234**, 367 (1931), **235**, 185 (1931); *Kolloid-Z.*, **50**, 39 (1930), **58**, 209 (1932); *Kolloid-Beihefte*, **36** 429 (1932); **43**, 143 (1935), **43**, 213 (1936); *Proc. Acad. Sci. Amsterdam*, **32**, 849 (1929), **44**, 1099, 1104 (1941), **45**, 59, 490 (1942); *Rec. trav. chim.*, **53**, 163, 171 (1934), **54**, 1, 17 (1935) and numerous others.
Note: *No attempt is made here to review the work of these authors on significance of coazervation in biocolloids.*

complex may be observed over a range of concentrations. In most cases this complex is a liquid, separating out in the form of microscopic droplets which after a time may unite to form a viscous liquid layer at the bottom of the container. The coazervate may range from a fairly fluid to a more or less liquid mass. Instead of gum arabic the electronegative colloid may be agar, lecithin or others, and in place of gelatin, the electropositive colloid may be serum albumin, egg albumin, casein or others, provided that the pH is held within required limits. When the two hydrophilic colloids of opposite signs are mixed there is a marked tendency for the two to approach and their electric double layers discharge each other, tending to cause a coprecipitate. The water of hydration, however, may prevent coagulation and the result is a weak union between the oppositely charged particles. At pH 1.2 the electric charge on gelatin and gum arabic is greatly diminished and separation ceases. Electric discharge of both colloids may also be brought about by addition of sufficient electrolyte, *e.g.*, KCl, which then inhibits the separation. For electrical equivalent concentrations the suppression of separation increases with the valence of the anion, *e.g.*, $KCl < K_2SO_4/2 < K_3Fe(CN)_6/3 < K_4Fe(CN)_6/4$, and of the cation, *e.g.*, $KCl < BaCl_2/2 < CoCl_3/3$.

Whereas the separation of gum arabic-gelatin is reversible for example by addition of electrolyte combinations, serum albumin is irreversible, probably due to a denaturation of the protein. A coazervate, on the other hand, may be found by the addition of a polyvalent ion to a hydrophilic colloid, even though the polyvalent ion and the colloid are not of opposite charges. This phenomenon, called autocomplex coazervation, is illustrated by the separation resulting from mixing solutions of a hexol salt of cobalt and gum arabic. Desolvating agents such as ethyl alcohol and acetone also increase the tendency to autocomplex coazervation. The term "simple coazervation" is employed where only one type of colloidal particle is involved and "complex coazervation" where more than one type is concerned.

The viscosity of coazervates is less than that obtained by averaging the viscosities of the components and, in general, the decrease in viscosity is proportional to the extent of coazervate formation. Incidental to their union the colloids lose water of hydration, that is, water is squeezed out between the particles and the viscosity is lowered. It is interesting in this connection to note that Rowson[25] found that the viscosities of mixtures of solutions of gum arabic and tragacanth, both of which are negatively charged, are lower than either of the component solutions.

According to Pauli, Russer and Schneider,[26] on the removal of about

[25] J. M. Rowson, *Quart. J. Pharm.*, **10**, 404, (1937).
[26] W. Pauli, E. Russer, and G. Schneider, *Biochem. Z.*, **269**, 158-74 (1934).

0.9 of its ash content by electrodialysis, gum arabic loses its protective action on highly purified Congo blue or gold sols. Restoration of the protective action can be accomplished by addition of the ash but neutralization of the electrodialyzed gum arabic with sodium or calcium hydroxide does not restore the protective action. Magnesium oxide addition does, however, restore protection.

Gum arabic lowers the surface tension of water. Clark and Mann[27] report the data for surface tension of solutions at 25°C.

Concentration of Gum Arabic Solutions %	Surface Tension in dynes/cm.
0.1	72.3
0.5	72.18
1.0	72.04
5.0	69.69
10.0	61.49

[27] G. L. Clark and W. A. Mann, *J. Biol. Chem.*, **52**, 178 (1922).

Chapter 3

India Gums—Ghatti, Karaya and Others

Gums of varying natures collected in different parts of India constitute an important portion of the world's production and specifically a large part of the American consumption. The gums from the genus *Anogeissus* of the family *Combretacae* include the species *Latifolia* which is widely distributed in India and in Ceylon. This is the tree which yields ghatti as it is more specifically known. Another important group of gums is collected from the genus *Sterculia* and specifically from *Sterculia urens*. The dried exudation from these trees enters commerce and the American market as karaya. It is to be noted that in most cases the India gums are the exudations of large-sized trees, while the arabic and tragacanth group of gums are collected from small thorny trees which in some cases approach bush-like character.

Because of their importance, ghatti and karaya are specifically discussed inasmuch as these are two of the few which have reached the stage of continuous commercial collection, grading, and organized trading on a recognized quality basis.

There are a number of other gums, usually produced in small quantities and sold under the designation of Indian gums. These are discussed from the botanical viewpoint and include among others the terminalia gums while the gums from various species of acacia which grow in India are discussed in connection with gum acacia and arabic.

Gum Ghatti

Ghatti gum, also known as Indian gum and Ghati gum, is a gummy exudation from the stem of *Anogeissus latifolia* Wall. The genus *Anogeissus* (*Fam. Combretacae*) includes four or five different species of tropical trees. Of these *A. Latifolia* is widely distributed in India and Ceylon. The tree is large and its leaves are rich in tannins and are used for tanning in Bombay. The gum is collected in April.

Ghatti gum should not be confused with either Bassora or gum Sterculin each of which is sometimes referred to as "Indian gum." Bassora gum is a collective term to indicate a group of highly colored gums somewhat resembling tragacanth. A gum of this class originally came into commerce from the neighborhood of Bassora on the Gulf of Persia. The

two principal commercial Bassora gums are pale-colored members of the class known as Indian gum and gum kuteera. Indian gum is obtained from *Cochlospermum gossypium* DC. (*Fam. Bixaceae*), a tree indigenous to southern Asia. One gram of gum added to 50 cc. of water forms an uneven mucilage which contains a few reddish-brown to yellowish-brown fragments. Upon stirring, the mucilage separates in the form of coarse uneven strings. Gum kuteera is obtained from *Sterculia urens Roxb.* (*Fam. Sterculiaceae*) a tree indigenous to southern Asia, abundant in sub-Himalayan tracts from the Ganges eastward and in Iran. It is inodorous, yellowish-brown tears or irregular masses and swells in water. Gum Shiraz is sometimes also confused with ghatti gum. There are two broad groups of gum Shiraz, (1) a gum from Iran, (the gum Shiraz) not being used in the United States, and (2) a product from India which is a mixture of the gum Shiraz and a number of fruit gums (peach, apricot, etc.), which are similar to ghatti. The gum Shiraz from India is sometimes used in textile printing.

Ghatti gum appears on the market in several variations, with a wide range of properties and appearance, *e.g.*, vermiform or rounded tears of varying size, colorless or pale yellow. The principal grades used in the United States are "ordinary" or "insoluble" and "superior" or "soluble." Actually none are totally soluble, but by means of an autoclave the gum may be made soluble. Poorer grades are not exported but used in India. Ghatti gum may be distinguished from gum arabic by its dull surface, uniform vitreous fracture and by the frequent presence of vermiform tears. It has a slight odor and an insipid taste; it is not entirely soluble in water. It forms a viscous, adhesive mucilage, more viscous and less adhesive than gum arabic. It is insoluble in (90 per cent) alcohol. Its aqueous suspension is gelatinized by addition of alcohol (90 per cent) or by a solution of lead subacetate, but unaffected by solutions of ferric chloride or lead acetate. It is not colored blue by iodine solution, indicating absence of starch and dextrin.

E. H. Shaw, Jr., and his students[1] have published several papers on the chemistry of gum ghatti. The gum was found to be 90 per cent soluble in water. The soluble portion which contained 0.72 per cent nitrogen, consists of a calcium salt of a polysaccharide acid, ghattic acid. The molecular weight of the soluble portion is about 12,000 as determined by osmotic pressure measurement. Free ghattic acid isolated by alcoholic precipitation has an equivalent weight of 1735. It contains 50 per cent pentosan, and at least 12 per cent of galactose or galacturonic acid. On hydrolysis of gum ghatti with sulfuric acid the specific rotation changed

[1] E. H. Shaw, Jr., et al., *Proc. S. Dakota Acad. Sci.*, **15**, 46 (1935); **16**, 34 (1936); **17**, 27 (1937); **19**, 130 (1939); **21**, 78 (1941).

from +42° to +58°. From the hydrolysis mixture, *l*-arabinose was isolated together with the barium salt of an aldobionic acid, pH 3.2, equivalent weight 352. Gum ghatti dialyzed from its solution in approximately normal sulfuric acid solution until sulfate free, gave a pH of 2.9. Electrometric titration with sodium hydroxide and hydrochloric acid gave an equivalent weight of 1340, corrected to an estimated pH 1.7 for the lower limit of the titration curve for the gum.

Carhart and Shaw in a study of coagulation of Prussian blue sols and Prussian blue protected by gum ghatti sols, report pH as an important factor in the coagulation. The influence of pH is due to its effect on the gum ghatti. In strongly acid solutions at pH's below its buffering range (2.7 to 5.5), the gum is a neutral colloid. As the pH is raised, the gum is converted to the sodium salt which is a negative colloid. Çataphoresis experiments showed the unprotected Prussian blue was an electropositive colloid. Prussian blue in gum ghatti solution at pH 0.8 was electropositive, the cataphoresis experiment showing an interesting phenomenon. During the course of the first few hours, the Prussian blue-gum ghatti micelle was electropositive and moved toward the negative pole. Twenty-four hours later the colloid showed definite stratification in rings 2 mm. thick and 3.5 mm. apart. The electrolysis of the small amount of KCl present had produced a definite pH gradient between the poles. Assuming the Prussian blue particles to be positive and the surrounding layer of gum to be negative, it is possible that at lower pH there is only a slight difference in charge between the two. The micelle, being slightly positive, migrates towards the negative electrode where it comes in contact with a relatively more alkaline medium (from the KOH), which favors the acquisition of more negative charges by the gum. This neutralizes the micelle which remains stationary, along with many other micelles, forming the rings. At pH 5.4 the gum ghatti is electronegative as are also the Prussian blue-gum ghatti micelles and the latter are stable towards agents which precipitate the Prussian blue containing no protective colloid. The isoelectric point, i.e., the point at which the micelles do not migrate to positive or negative poles, of the Prussian blue gum was found to be between pH 2.2 and 1.4, probably at 1.7. The most satisfactory range for coagulation by KCl of the gum-protected blue sol was found to be between pH 2.2 and 3.3. Above pH 4.2, the colloid was completely stable to saturated solutions of KCl.

The uses of gum ghatti are similar to those of gum arabic. In India and certain other parts of the British Empire it may be employed in making official preparations for which gum acacia is directed to be used, one part of ghatti replacing two parts of acacia in a number of pharmaceutical preparations.

KARAYA

Gum karaya has become an important raw material in the textile, cosmetic, food and other industries. It resembles gum tragacanth in that it swells in cold water to form an opaque gel. Karaya gum has been used in the United States since the latter part of the 19th century, but the large scale use in the United States dates from World War I, when the price of tragacanth was high. Karaya is frequently sold as tragacanth and undoubtedly, even before World War I, some of the gum sold as tragacanth was really karaya. Karaya gum imports into the United States are far in excess of those of tragacanth, usually more than double. Karaya is less expensive than tragacanth, and is superior for certain purposes.

United States' imports in 1939 were in excess of 7,600,000 pounds with a declared value at the port of export of $575,000.

Gum karaya is the dried exudation from trees of the *Sterculia urens*, a native tree of India, which is found chiefly in Gujerat, the central provinces and to some extent in the Central Indian Agency.

In the United States it is known as gum karaya, gum kadaya, Indian tragacanth, India gum (not to be confused with Indian gum which is another name for gum ghatti) and *Sterculia*[2] gum. In India the gum is known by the names karaya, kadaya, katilo and kullo. India is the sole source.

The trees from which karaya is obtained (unlike those that yield gum arabic and gum tragacanth) are big, reaching a height of 25 to 30 feet, and their trunks are large with a soft corky structure. The trees grow in sizable forests which are for the most part government owned, but many are on privately owned estates. The gum is obtainable throughout the year except in the rainy season, and the best quality is obtained during the hot spell, which is from March through the middle of June. Usually five or six incisions per tree, each incision about two feet long and deep enough to reach the heartwood, are made in the trunk by the natives. Sap or juice oozes out and collects in large irregular knobs in the incisions. The knobs are dug out in about three days and new accumulations grow in the same incisions. If the gum is not collected the wounds heal and fresh incisions in new places must be made. Trees generally yield gum for eight or nine months, then cease for two or three years after which they may again be tapped.

The gum is collected by natives usually when there is a scarcity of

[2] The Condensed Chemical Dictionary (Reinhold, 1942) defines Sterculia gum as a series of gums obtained from the genus Sterculia found in India, Africa and Australia, similar to tragacanth in appearance, but with a variation in properties. Some of these gums have great adhesive properties while others have great swelling power in water, but poor adhesive qualities.

other work. It is taken to the villages where the merchants sell it to dealers in Bombay where sorting and grading is done, generally by women. Figure 11 shows the preliminary sorting and classification and Fig. 12 illustrates the final grading. The large lumps are broken up with stones and sorted in piles according to color and freedom from bark and other impurities. The best grades are white, the poorest are dark brown to black.

FIGURE 11. Preliminary sorting karaya gum, Bombay, India. (*Courtesy The Philadelphia Commercial Museum*)

Toothaker[3] describes kuteera gum as the product of a large tree, *Sterculia urens*, in India. He states that a similar gum is yielded by *Sterculia foetida*. Still similar gums of the same general appearance are produced by *Sterculia tomentosa* and *Sterculia cordifolia* in the region of Senegal, West Africa and adjacent territory. In reference to these particular sterculia gums, they are yellowish to brownish in color and sizes, with dimensions approaching two inches or better in their largest portion.

[3] C. R. Toothaker, "The Soluble Gums," No. 4, Handbooks to the Exhibits to The Commercial Museum of The Philadelphia Museums, Philadelphia, Pa., 1921.

In their raw form the gums are acid in nature and some samples are observed to give off acetic acid upon exposure to moist air. They swell up in cold water according to Toothaker and form a loose, flocculent, opalescent jelly. Their acidity restricts their demand. It is probable that when they are collected under proper supervision and adequately graded, they fall in the karaya class and are used in the same manner as karaya.

There are a large number of grades of karaya, each shipper, inspector and dealer using his own group of designations. Weighing and bagging, a manual operation, is shown in Fig. 13 with typical shippers' grade mark-

FIGURE 12. Selecting and sorting karaya gum, Bombay, India. (*Courtesy The Philadelphia Commercial Museum*)

ings. Although the products that enter the country are chiefly irregular tears, practically all that is sold to consumers is powdered, much of the bark being separated after powdering by an air blast which removes the bark, which has a lower density than the gum. Colors vary from white to gray and are often reddish. The gum is powdered for an additional reason. If it is unpowdered, addition of water yields a non-homogeneous

colloidal solution. If finely powdered, each particle swells and the appearance and behavior of the solution is more like a homogeneous solution. It is believed that the poorer grades are usually more acid and swell more.[4] By means of an autoclave, the gum may be made soluble in water, and the solubilizing is sometimes so done by consumers. By this means, it more readily approximates the more soluble gums which it has largely replaced.

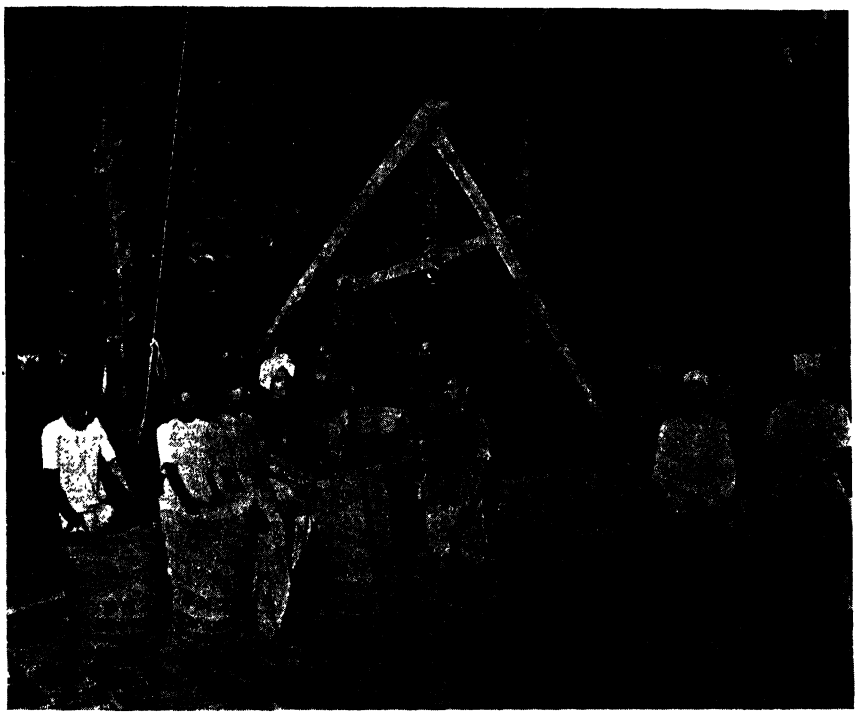


FIGURE 13. Weighing and bagging karaya gum, Bombay, India. (*Courtesy The Philadelphia Commercial Museum*)

Although the knowledge of the chemical structure of karaya gum is meagre, there is some information which sheds light on its chemical makeup and behavior.

The chief chemical constituent is the galactan gelose. The gum usually has the odor of acetic acid, and Peyer in 1925 reported also the presence of the odor of trimethylamine. Thrun and Fuller[5] treated samples of the gum with sodium hydroxide, and by Kjeldahl determinations found

[4] Stallman & Company, New York, private communication.
[5] W. E. Thrun and H. V. Fuller, *Ind. Eng. Chem.*, **27**, 1215 (1935).

the amount of volatile base to be equivalent to 1.1 to 1.2 cc. of N/10 alkali.

The gum shows an acid pH when in contact with water, and electrophoresis experiments show the gum to be a negative colloid. Addition of sulfuric acid or phosphoric acid to karaya solutions followed by distillation yields a volatile acid, at least a large part of which is apparently acetic acid. Flück[6] reports the volatile acid number varies from 13.4 to 21.3. Thrun reports 17.4 to 22.7. Expressing the latter results in terms of equivalent cc. of N/10 alkali, it is 4.5 to 5.8 cc. Thrun found that the amount of acid washed out of 1 gram of karaya using absolute alcohol as the extracting agent was equivalent to 3 cc. of N/10 alkali. Gabel[7] added glycerine and water to karaya and titrated with N/10 alkali using phenolphthalein as an indicator. He reported an acidity equivalent to 4.5 cc. alkali per gram of gum.

Thrun[8] has shown that pH (and titrations) of karaya solutions must take into account method of titrating, adsorption of dye if the pH is taken colorimetrically, time and method of adding solutions to the gum. He found that pH of gum solutions determined electrometrically, with quinhydrone, becomes higher after 24 hours. The apparent pH taken colorimetrically agrees at first with that obtained with the quinhydrone, but if the indicator is added to the water used in preparing the solution the color remains constant. If a small amount of ammonia is added to the indicator solution and this added to the gum, the pH measured electrometrically and colorimetrically both show a decrease as the solution ages. Typical pH taken over a period of time by means of indicators and electrometric measurements are shown in Table 5.

Table 5. Colorimetric and Quinhydrone pH Values
(*1% solutions; indicator added to water before solution*)

	No Ammonia		Ammonia Present					
Time Hours	(a) Bromocresol pH.	(b) Green Quinhydrone pH.	(a) Phenol Red pH.	(b) Red Quinhydrone pH.	(a) Phenol Red pH	(b) Red Quinhydrone pH	(a) Cresol Red pH	(b) Red Quinhydrone pH
0.8	4.6	4.63		9.42		8.77		8.56
3.2	4.6	4.62		9.03		8.58	8.5	8.50
23.5	4.6	4.64	8.3	8.72	7.7	8.02	7.7	7.99
29.5	4.6	4.71	8.1	8.50	7.4	7.53	7.3	7.22
50.0	4.6	5.03	7.8	8.14	6.8	7.10	7.0	7.00
76.0	4.6	5.13	7.7	8.14				

(a) Colorimetric pH
(b) Electrometric pH

[6] H. Flück, *Pharm. Acta Helv.*, 3, 151 (1928).
[7] L. F. Gabel, *J. Am. Pharm. Assoc.*, 23, 341 (1934).
[8] W. E. Thrun, *Ind. Eng. Chem.*, 27, 1218 (1935).

Thrun explains the divergency by assuming that the gum particles adsorb the indicator and are themselves more acid than the solution in which they are suspended, that the quinhydrone value gives the pH of the solution while the indicator after sufficient time gives the pH of the particles. As acid is adsorbed from solution by the particles in the first example, the quinhydrone pH rises after a time. Thrun adds further evidence to substantiate this theory by measuring the quinhydrone pH values from solutions prepared by dissolving in 0.05N acetic acid and taking pH readings 24 hours later. The results in Table 6 show that the gum, although acid itself, raises the pH (that is, lowers the hydrogen ion concentration) of the external acetic acid solution.

Table 6. pH of Karaya Gum Dissolved in 0.05*N* Acetic Acid

Grams—gum per 100 g. Solvent	Quinhydrone pH at 25°C
0.0	3.10
0.2	3.50
0.4	3.56
0.6	3.58
0.8	3.64
1.0	3.69
1.2	3.76
1.4	3.84

Thrun measured the pH of solutions of karaya (Table 7), one set of solutions being made slightly ammoniacal at the time the gum was dissolved, the other set made ammoniacal with the same amount of ammonia, but four hours after the gum was dissolved. The pH of the slightly ammoniacal solutions drops because of the gradual release of the acid by the particles which themselves remain more acid for some time. The pH in the second set was higher than that of the first set in each case. Thrun explains this behavior as showing that the gum particles had adsorbed acid in the first four hours, and that this acid had not immediately been given up to neutralize the ammonia. It would seem likely that while this explanation sounds reasonable, there is at the same time a diffusion (or adsorption) of the ammonia into the gum as well as a diffusion of released acid from the gel to the external solution.

Thrun states that the differences in pH of the particles and the surrounding solution, the changing pH and the swelling of the particles point toward the establishment of a Donnan equilibrium.

Viscosity. The viscosity behavior of karaya solutions reflects its usefulness in most of its applications more than any other single property. There have been several interesting viscosity relationships reported in

Table 7. Quinhydrone pH of Solutions Containing 0.665 Milliequivalent of Ammonia per Gram of Gum

Grams of Gum per 100 g. Solvent	NH_3 Added to Solvent H_2O, pH	NH_3 Added 4 Hours after Solution, pH
0.2	7.90	8.15
0.4	8.03	8.35
0.6	8.07	8.29
0.8	7.50	8.02
1.0	7.74	8.21
1.2	7.25	7.90

the published literature, but there remains much to be studied in this field.

Karaya particles imbibe large amounts of water to swell to great size, but they do not dissolve or form homogeneous suspensions unless ground extremely fine or subjected to treatment in an autoclave. The latter treatment does "solubilize" to the extent of yielding a water-soluble gum like gum arabic, but viscosity relationships of such "solubilized" gums have not been published as far as known.

The degree of water absorption and viscosity of gum karaya varies widely with different shipments. Although it is generally assumed that viscosity is affected by the season of the year in which the gum is tapped and collected and conditions of growth, there is no assurance that the product of any one section of India or of any particular season of the year will produce a high-viscosity gum. The larger dealer tests each shipment and blends it with other shipments to make standard grades where possible.

As already pointed out karaya gum is ground before it is made into a suspension in water. The importance of fine grinding is demonstrated in Table 8.

Table 8. Effect of Grinding of Gum[9]

Per Cent of Gum in The Water Dispersion	Screen Size of Powdered Gum	Properties of The Dispersion
2	200 mesh	Coherent mass, flows easily
4	200 mesh	Thick and viscous, adheres to glass
2	100 mesh	Separates in clumps
4	20-30 mesh	Full of air bubbles, slides freely and has free water
4	5-20 mesh	Free water visible that can be drained off.

Thrun and Fuller showed the very rapid rise in viscosity of karaya suspensions with increase in concentration. The results are tabulated in

[9] C. F. Mason, *Chem. Ind.*, 53, 858 (1943).

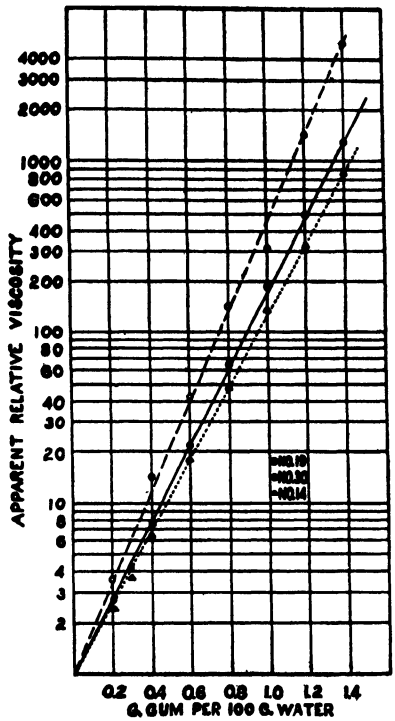


FIGURE 14. Logarithm of increase in apparent relative viscosity *vs* concentration.

Table 9 and plotted in Fig. 14. Three samples of karaya were used. Number 19 was a typical high grade gum containing no brown masses and a few crystal-like masses, number 30 was a very high grade gum containing no crystalline masses and a large number of feathery masses, and number 14 was a fairly good grade but had more brown and crystal-like masses.

Table 9. Viscosities of Gum Karaya Dispersions in Water at 25°C.

Grams of gum in 100 g. of water	Apparent Relative Viscosity of Three Separate Samples		
	No. 19	No. 30	No. 14
0.2	3.70	4.53	3.39
0.3	5.25	7.23	4.87
0.4	8.75	14.50	7.32
0.6	22.00	43.60	18.95
0.8	63.30	134.00	48.20
1.0	178.00	303.00	137.00
1.2	495.00	1,413.00	348.00
1.4	1,280.00	4,060.00	875.00

Dispersions stood 24 hrs. before measurements were made.

Karaya gum solutions are not finely divided homogeneous suspensions. They contain relatively large irregularly shaped masses that swell up and tangle with one another to give a high resistance to flow. The logarithm of the increase of viscosity over that of water is, according to Thrun and Fuller, proportional to the concentration. The relation may be expressed by the equation—

$$\log\ (\eta_s - \eta_0)/C = K$$

where

η_s = relative viscosity of the solution

η_0 = viscosity of water = 1

C = concentration of gum in grams per 100 grams of water

K = a constant.

The relative efficiencies of different samples may be obtained by reading from the curves or by calculating amounts of gum required to give the same relative viscosity.

These authors describe apparatus, procedure and logarithmic relationship which have been used in evaluating gums offered for sale or received. Their apparatus is pictured in Fig. 15. By using interchangeable capillarics of various lengths and bores which are calibrated to give relative

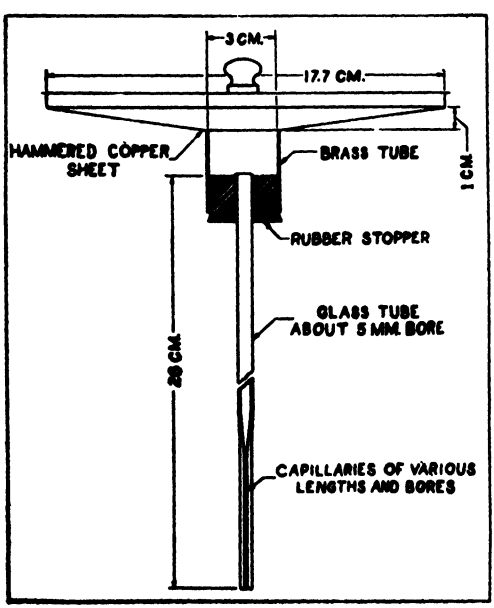


FIGURE 15. Viscosimeter for karaya gum solutions.

viscosity of water it was possible to use fairly wide bores for the more viscous solutions and narrow bores for less viscous solutions. In this way, the danger of turbulence was eliminated. Calibration of the tubes was carried out in the following manner. The time required for 10 grams of solution (or water) to flow through the tube was measured in all determinations. A tube of narrow bore (tube #1) was used to measure the time of flow for water and for a dilute solution of gum. The time of flow for the dilute solution was then determined using a tube (#2) of wider bore. Water run through tube (#2) would experience turbulence but the dilute gum solution does not. It is possible then with the data obtained to calculate the non-turbulent viscosity of water in tubes. Employing a more concentrated gum solution, time of flow is determined in tube (#2) and in a tube (#3) of a still wider bore and the relative viscosity of water in tube (#3) calculated therefrom. In this way relative viscosity without turbulent flow can be obtained over a wide range of viscosity.

Gabel[10] measured viscosities of karaya and tragacanth solutions using a MacMichael viscosimeter and reports that karaya solutions are not as thick as tragacanth, that karaya solutions become thinner with time and that heating the karaya solutions reduces their viscosity. Neutralization of karaya with potassium hydroxide causes it to be stringy and tends toward lowered viscosity with ageing and heating. These results and supporting data are given in detail in the chapter on gum tragacanth.

Glarum[11] using a Stormer viscosimeter demonstrated that mucilages of karaya, like tragacanth and thick textile printing color pastes, show with increasing load a sharp rise in fluidity, which is measured in revolutions per second divided by the load. The increase in fluidity is not as rapid as that of tragacanth and accordingly would not have as false a body as the tragacanth. The viscosity of gum arabic, on the other hand, shows a constant fluidity with varying loads.

Indian Gums

Many other tropical trees produce gums which are collected locally and when sufficient in amount reach the export market. When there are insufficient amounts, gums from different trees may be lumped together to give irregular shipments of non-reproducible quality. The chemistry of these gums is little understood and at times their botany is the subject of dispute. The appellation "Indian gum" or "East Indian gum" is one of confused terminology. Occasionally distinctly named and generally rec-

[10] L. F. Gabel, *J. Am. Pharm. Assoc.*, **23**, 341 (1934).
[11] S. N. Glarum, *Am. Dyestuff Reptr.*, **26**, 124 (1937).

ognized parcels of particular gums reach the market and for this reason they are classified here.

The dhak or palas tree, *Butea frondosa,* grows widely in the forests of India. It yields a dark red gum which ordinarily contains some tannin. It is a hydrophilic colloid but most of its application is local. There are no recognized gradings.

The chittagong tree, *Chickrassia tabularis,* produces a water-soluble reddish to amber-colored exudation which sometimes reaches the market as an admixture in Indian gums.

The wood apple tree, also known by the natives as the elephant tree, *Feronia elephantum,* yields a yellow to reddish soluble exudation which is collected locally and employed in native industries in connection with dip dyeing and coloring.

Trees of the species *Melia azadirachta,* classified by some botanists as *Azadirachta indica,* are tapped and the amber-colored gum collected therefrom to become a component of some of the East Indian gums. Its quality is not equivalent to that of ghatti.

Moringa gum is from *Moringa pterygosperma* which is called the horse radish tree by the natives. Collection is irregular and there is a question as to whether the tree exudation is a true gum or a mixture of gums and resins. It has some local application in connection with batik dyeing.

Several species of terminalia such as *Terminalia arjuna, Terminalia bellerica, Terminalia catappa, Terminalia chebula, Terminalia tomentosa,* are tapped for yellowish to reddish gum exudations by native collectors who sell them to traders. These terminalia materials in certain areas are important contributors to the crude East Indian gums. Ordinarily these gums are inferior in their thickening or adhesive powers to medium grades of ghatti, karaya, or tragacanth.

The East Indian varieties of acacia have been discussed in connection with gum arabic.

The siris tree, *Albizzia lebbek, Albizzia amara, Albizzia odoratissima, Albizzia procera, Albizzia stipulata,* a small thorny shrub-like growth, is fairly widespread in India and the Far East. It yields a yellow to brown hydrophilic gum which swells readily and forms soft clear jellies. The gum is occasionally met as an admixture in the poorer grades of arabic.

The cashew family, *Anacardiaceae,* was originally a native of the American tropics, particularly Brazil and the West Indies. It was introduced into the Far East by the Portuguese and is now found widely throughout the Orient. The tree is a dome-like evergreen growing to a height of 30 to 40 feet, often with a spread of 60 feet. It is best known as the source of the cashew nut which is an article of commerce and the im-

portant paint material cashew nutshell liquid.[12] The tree yields from 5 to 12 pounds of a water-dispersible gum which may be collected when the sap is rising. The gum exudes from the bark, and locally finds application for many pharmaceutical purposes as well as a substitute for gum arabic. It is stated that it has good properties as a mucilage and is particularly valuable as a coating to protect against the depredations of insects. Applicationwise, the gum is not a competitor of gum arabic in that it shows incomplete solubility in cold water, but the undissolved part disperses to form a soft clear jelly. The color of the gum is usually dark red. The antiseptic or protective effect is associated with the natural phenolic type compounds which play such an important part in cashew nutshell liquid applications.

Mahua gum from *Bassia longifolia* and semla gum from *Bauhinia retusa* and *Bauhinia variegata* are collected locally in different districts in India and to some extent are used in food preparations. Their qualities are relatively poor.

Chironji gum is obtained by tapping, accidentally or intentionally, the *Buchanania latifolia*. In some respects this gum resembles karaya and when available in large enough amounts may reach the market under a karaya designation.

Kino gum is from the tree *Pterocarpus marsupium*. When separate it is usually dark red in color, is partly soluble and forms a soft jelly. Commonly, however, gum kino is another name for dragon's blood which is a resinous substance obtained from the fruit of several species of small palms growing in the East Indies. Dragon's blood is not a gum but a gum resin and its commercial value depends upon its insolubility in water and its solubility in organic solvents.

Soap-nut tree gum, locally known as ritha, comes from the tree *Sapindus trifoliatus*. It shows hydrophilic colloidal properties to a limited extent, but the gum is often contaminated by other products from the tree. It finds local usage in native arts and industries, but rarely enters international trade except in some specialized pharmaceutical applications.

The gums of *Cochlospermum gossypium*, according to Robinson,[13] yield 14 per cent of acetic acid upon distillation. These gums lose 19 to 21 per cent of their weight on heating at 100°C. and show mineral contents of 7 to 9 per cent. They require 13 to 16 per cent of their weight as potassium hydroxide for neutralization. They contain galactan and araban, but less of the former than in gum arabic. It is probable a third carbohydrate

[12] Frederick M. Damitz, Protective and Decorative Coatings, Vol. I, Chapter 2, edited by J. J. Mattiello, John Wiley & Sons, Inc., New York, 1941.
[13] H. H. Robinson, *J. Chem. Soc.*, **89**, 1496 (1906).

exists. They swell up very quickly on treatment with water to form nearly transparent gels which, however, are so brittle that they can be pulverized by gentle rubbing into a very large number of minute angular particles. After rupture these particles do not further coalesce. The gum is of interest scientifically but has no commercial value in comparison to other materials.

Chapter 4

Gums from the Astragalus Plant

Tragacanth and Persian Gums

The small thorny shrubs of the various species of *Astragalus* grow in semi-desert places. These shrubs yield gums which swell in cold water forming a thick and ordinarily transparent jelly. After a swelling period of several hours, these jellies may be shaken up with many more volumes of water to form a strong mucilage or adhesive material. As a class, the gums from the *Astragalus* are more opaque than those from acacia species of plants. The gums are less brittle, less glassy, and ordinarily in their commercial forms show a luster which is duller than gum arabic for example.

The species which yield gums are numerous. Typical of them are *Astragalus adscendens, Astragalus leioclados, Astragalus brachycalyx, Astragalus gummifer, Astragalus hamosus, Astragalus microcephalus, Astragalus pycnocladus, Astragalus stromatodes, Astragalus kurdicus, Astragalus verus, Astragalus parnassi, Astragalus cylleneus.* Perhaps the best known commercial name for the gums from *Astragalus* is tragacanth.

The Persians refer to the plant from which gum tragacanth is obtained by the name "Gavan."

There is a paucity of reliable observations and experimentations to explain the formation of the gums from the astragalus shrubs. In 1860 Hanbury reported in the Pharmacographia, written by Flückiger and Hanbury, that when a branch of the shrub of the thickness of a finger is cut, an exudation occurs from the center with the formation of a stream of soft gum pushing itself out like a worm.

A British Consular Report of 1903 to 1904 on The Trade of Kermanshah states that first quality katya (one of the many Persian names for gum tragacanth) is the result of cutting the branches of the "Gavan-sefid" which is the white gavan, while second quality is obtained from the larger yellow gavan after the top is burnt and the incisions made after the fire has consumed all of the leaves. Another variety termed "arrehbor" is a gum which is formed at the points where branches of a small tree are cut with a saw, the cutting being done after the top of the tree has been burnt.

TRAGACANTH

The annual United States consumption of gum tragacanth from 1929 to 1940 averaged about 2¼ million pounds, being chiefly imported from Iran and Turkey, with imports also from Russia, Irak, British India, Syria and Palestine. Prior to the World War I, Turkey was the most important source, but for many years now Iran has supplied the greatest amounts and its products are superior.

Gum tragacanth appears on the market chiefly as ribbons and flakes, though irregularly oblong or roundish and tortuous vermicular shapes, powder and aqueous solutions are also offered to the trades, the latter for certain specialized uses and generally treated to endow it with desired specific properties. The ribbons and flakes are horny, translucent and possess short fracture. Tragacanth may be more easily pulverized by heating to 50°C. Color varies from white to light brown. Specific gravity of different samples varies, e.g., one worker reports 1.25, another 1.384.

The grades offered for sale are very numerous and grading leaves much to be desired. Purchase from the same supplier and based on samples offered is the general rule. The white leaf gum, also called Syrian tragacanth, obtained in Kurdistan and Iran is the best grade on the market. Smyrna tragacanth usually appears as broad thick opaque flakes, yellowish or brownish. The ordinary tragacanth, tragacanth in sorts, known as tragantors or common tragacanth occurs in irregular pieces. U. S. P. (*Astragalus gummifier*), Aleppo numbers 1 to 6 depending on quality, "extra select" and similar designations are also employed.[1] Because of its high price, tragacanth is sometimes adulterated with poorer gums and whitened with lead carbonate.

Tragacanth is one of the oldest drugs in Materia Medica and its commercial use dates far back. It was known in the days of Theophrastus, who described it three centuries before the Christian Era. It has been official in every edition of the U. S. Pharmacopoeia since 1820.

There is little scientific evidence, nor has there been much study concerning the formation of gum from the *Astragalus* shrubs. It appears that tragacanth is the result of some alteration or metamorphosis of the soft juicy cells of the plant. The gum is not simply the dried juice differing in this respect from resinous exudations, in that examination under the microscope shows many cells in the stage of the transformation process. The altered cells, or those undergoing transformation, are largely in the

[1] Tragacanth gum is known in Iran (Persia) and frequently in Afghanistan and in India as katira, katyra, kathira, katad, kettira, kutera, chitira and halusia. In India other gums are sometimes sold under the name of katira, more particularly karai, or karaya gum and katira-i-hindi or Hindu tragacanth.

pith portions of the wood. It also appears that the alteration into gum does not take place in the young or fresh growth, but only in the older stems, the bottom portions of the shrub, and the older branches. There appears to be little evidence to indicate that the transformation of the cells is the result of bacterial action, although there is no conclusive evidence against this.

When the stem of the plant is cut deeply with a knife and the incision is near the root and as deep as the pithy portion, flake gum is formed. These are gathered after drying on the plant for three or four days. The vermicelli or worm form originates from stems which are cut entirely across. The lump form occurs at natural breaks in the bark and is in roundish tears or globules.

The shrubs are plentiful over all of the mountains of southern Iran and the entire mountainous region which runs northwest along the Mesopotamia district and including areas like Arabistan, Kurdistan, and adjacent territory. In the Bagdad area, Suleimanaya is an important collecting center, as is Bagdad for the trade. Syrian tragacanth ordinarily comes from Iran and Kurdistan, and Smyrna is an important wholesale market where the gum is sorted and classified before it is shipped to European distributing points in Trieste, Bordeaux, London, and Hamburg. It appears that gum tragacanth is not a secretion of the plant, but the result of the transformation of cells of the pith and medullary rays which traverse the ligneous part of the stem and older branches by a process known as gummosis. The gum swells by absorbing water and due to the pressure in the interior of the stem forces its way out through cracks or through incisions made to assist the exudation. Collection is in May and June in the warmer districts and somewhat later in the cooler areas, often in July, August or even September. The best gum is obtained in the cooler districts. Plants are tapped in their second year since the product obtained in the first year's growth is poor and unfit for commercial use. In Iran, in the Province of Fars[2] the earth is cleared away at the base of the plant to a depth of two inches and the exposed part incised with a sharp knife having a thin cutting edge, and a wedge-shaped piece of wood is forced into the cut to open the wound and thus permit freer exudation. The wedge is generally removed after 12 to 24 hours. The gum exudes and is collected 2 days after the incision is made. Some plants are partly burned and after the leaves are consumed, the fire is extinguished. This sickens the plant which then gives off a greater quantity of gum. The practice of burning is not universal as many plants cannot recover from this drastic treatment and the gum yielded is of poorer quality, is reddish

[2] G. E. Trease, *Pharm. J.*, **137**, 206 (1936).

and has a dirty appearance. Methods vary somewhat in different areas; for example, it is said that in the Kerman district the laborers use thick knives to the detriment and often to the destruction of the plant.

When the gum flows out of the incision it dries in the form it takes as it leaves the wound. If the incision is narrow and longitudinal, flakes or leaves result. If the weather is dry these are white and the "white leaf" form is the most highly prized. If it rains or there are wind storms which carry dust to the surface of the gum, the product loses its whiteness and is called "yellow leaf." The gum forced through rounded holes and drying in tears or vermiform pieces is called "vermicelli" tragacanth.

"Persian" tragacanth usually embraces the better grades from a number of areas, "Bagdad" or "Syrian" refers chiefly to gum which passes through Bagdad and is shipped through Basra. "Bushire" or "Persian" consists mainly of the gum from the Province of Fars, and is shipped from Bushire. In the Province of Fars, the villagers collect the gum and it is brought to Shiraz by pack animals. In the Kerman district the chief buying centers are Kerman, Sirjan, Pariz, Baft, Bam, Rohbur, Rawar, and Zarand. The gum is sorted at the coast for the local buyers by boys and girls into 7 qualities, the numbers 1 to 5 being exported while the numbers 6 and 7, the poorest, are used in Kerman and Yezd for stiffening cloth.

According to Delahanty and White[3] the Anatolian plateau of Turkey is the most important producing area of Turkey. The gum is sorted into several grades at Istanbul. There are also exports from Smyrna.

Although the amount of research on the chemical structure of tragacanth has been limited, a number of interesting observations have been made. Like gum arabic, gum tragacanth is of carbohydrate nature and has acidic components which are largely present as calcium, magnesium and potassium salt. In tragacanth the gum consists of a soluble portion, called "tragacanthin," and an insoluble portion, called "bassorin," the latter constituting 60 per cent to 70 per cent of the total. Norman[4] believes the soluble constituent to consist of a ring containing 3 molecules of glucuronic acid and 1 molecule of arabinose with a side chain of 2 molecules of arabinose. The soluble portion gives a colloidal hydrosol solution with water while the insoluble part swells to form a gel.

Introduced into water, gum tragacanth absorbs a large amount of the water and swells greatly to form a soft adhesive paste, but does not dissolve. If agitated with additional water, the paste forms a uniform mixture but after 1 or 2 days the greater part separates out and leaves the rest dissolved.

Tragacanth is wholly insoluble in alcohol. Its ability to swell in water

[3] Delahanty and White, "Commerce Report" (May 11, 1932).
[4] A. G. Norman, *Biochem. J.*, **25**, 200 (1931).

to form a gel of high water content (or conversely of low gum content) and the ability of these gels to give unique viscosity, emulsion stabilizing and demulcent behavior account in large measure for its extensive use.

Gabel[5] reports that tragacanth is acid in reaction and that 1 gram of the gum requires 0.9 cc. N/10 alkali for neutralization to phenolphthalein. Karaya gum requires five times as much alkali for neutralization.

Krantz[6] reports a pronounced buffer action between pH 3 and pH 10 as shown in Table 10. Weak gels (0.5 per cent) were prepared in water adjusted to different pH values.

Table 10. Buffer Action in Tragacanth Gels

pH of Solvent	pH of Gel	pH of Solvent	pH of Gel
0.04	0.04	6.48	5.88
0.95	0.96	7.86	6.82
1.92	2.10	9.75	7.70
2.88	3.81	10.47	9.99
3.93	4.93	11.85	11.50
4.78	5.54	12.74	12.68
5.80	5.56	13.65	13.65

Viscosity of tragacanth mucilages has received attention from many investigators. Different methods of measuring the viscosity have been studied and viscosity has been tried as a yardstick[7] for specifications and for a guide to behavior as a suspending agent and as an emulsifier. Demulcent action is also related to the high viscosity and other colloidal properties of the gum.

Gabel has compared the viscosity of tragacanth and karaya mucilages of different concentrations and with both a MacMichael viscosimeter and a pipette, the tragacanth being much more viscous. In one example, a 1 per cent tragacanth solution had approximately the fluidity of a 2 per cent karaya solution after 6 months' ageing.

Viscosity of tragacanth mucilages is reduced by adding acid, alkali and sodium chloride, particularly if the mucilage is heated. Schon and Fürst[8] found the viscosity is a maximum at pH 8, dropping sharply at either side. Gabel[9] found that a tragacanth mucilage will show in-

[5] L. F. Gabel, *J. Am. Pharm. Assoc.*, **23**, 341 (1934).
[6] J. C. Krantz, Jr., *J. Am. Pharm. Assoc.*, **18**, 471 (1929); **19**, 1181 (1930).
[7] Examples are found in the papers by G. Middleton (*Quart. J. Pharm.*, **9**, 506 [1936]) in which it is proposed that the relative strength of a sample of tragacanth be defined as that dilution which will give a test of 40 seconds under conditions described. A. B. Nichols (*J. Am. Pharm. Assoc.*, **26**, 823 [1937]) suggests that in order to develop a jelly of ephedrin sulfate NF of uniform viscosity that the tragacanth be required to pass a mucilage test based on time for a steel ball to fall a given distance through a mucilage of given concentration.
[8] S. A. Schon and W. J. Fürst, *Dansk Tids. Farm.*, **15**, 34-39 (1941).
[9] L. F. Gabel, *J. Am. Pharm. Assoc.*, **23**, 341 (1934).

creased viscosity if boiled, though not too long, and also on ageing, but a decreased viscosity if neutralized. His results are tabulated in Table 11 together with his results for karaya gum. Boiling lowers the viscosity of the latter.

Table 11. Viscosity of Tragacanth and Karaya Mucilages with MacMichael Viscosimeter

Gum	Ageing Periods and Treatments	Made Without Heat	Brought to a Boil	Boiled 2 Minutes	Boiled 5 Minutes	Boiled 10 Minutes
Group No. 1						
Tragacanth Aleppo No. 1	Original reading	17	19	39	61	61
	After 3 months	73	84	90	108	101
	After 10 months	93	117	140	120	115
Karaya Superior Grade	Original reading	14	35	20	21	25
	After 3 months	26	34	27	28	26
	After 10 months	20	19	15	15	10
Group No. 2						
Tragacanth Aleppo No. 1	Original reading	91	—	140	130	110
	Original reading*n	85	—	49	27	27
	After 2 months	128	—	140	138	117
	After 2 months*n	160	—	55	30	29
	After 4 months	145	—	150	150	120
	After 4 months*n	147	—	48	28	26
Karaya Superior Grade	Original reading	68	—	63	56	46
	Original reading*n	93	—	—	—	—
	After 2 months	59	—	63	60	55
	After 2 months*n	64	—	69	53	44
	After 4 months	35	—	45	40	33
	After 4 months*n	36	—	27	25	21

*n = Neutralized

Mechanical treatment also has an important effect on the viscosity of tragacanth. Schon and Fürst found that by passing a tragacanth mucilage through a homogenizer, the viscosity kept increasing. After four passages of the gum solution through the homogenizer, the viscosity reached a maximum.

Middleton[10] points out that hydrophilic colloids such as gum tragacanth owe their high viscosity to some form of structure in the liquid and if this structure is broken, the viscosity may be greatly reduced. If a solution shows a reduction in viscosity after shaking and an increase after being permitted to remain undisturbed, and the cycle can be continually repeated, then the solution is said to exhibit thixotropy. Gum tragacanth solutions do not show thixotropy. Middleton suggests that it is probable that these solutions show "stream double refraction," the orientation of colloidal particles along or in relation to the direction of the movement in the liquid. Even in filling the viscosimeter tube, it is hardly possible to avoid some degree of orientation in the liquid. Middleton found that

[10] G. Middleton, *Quart. J. Pharm.*, 9, 493 (1936).

passing the solution through a fine strainer, fine grinding, or storing caused an increase in viscosity.

Glarum[11] measured the viscosity of several gums, starches, castor oil, and a textile printing paste in a Stormer viscosimeter under different loads. For castor oil and gum arabic the fluidity (revolutions per second divided by the load) remained fairly constant. For gum tragacanth the fluidity increased 54 times for a load increase of six-fold. Such a material will give a shorter and more false body than the arabic.

Rowson[12] found that the addition of an acacia mucilage in any proportion to one of tragacanth results in a viscosity lower than that of either constituent mucilage. He explains the decrease in viscosity as a dehydration of the gel masses of tragacanth and their disposition as white floccules, the viscosity of the mixture being low. A minimum viscosity was attained in a mixture consisting of 80 per cent tragacanth mucilage and 20 per cent acacia. Similar results were obtained when these mixtures were diluted with 7 volumes of water and the viscosities and suspending powers measured, although a minimum value was found at a different concentration.

Rowson found that a small quantity of acacia in compounded tragacanth powder produces a reduction in viscosity and suspending power of the tragacanth either in the presence or absence of electrolytes. No similar reduction is brought about by the starch or sucrose present.

Evers and McLachlan[13] showed that the suspending power of gum tragacanth is not affected by nitrogen or ash content, is adversely affected by heating the dry gum to 100° to 120°C. or by grinding, and is brought to a more uniform strength more rapidly by heating the mucilage instead of allowing it to remain cold. Mucilages made in the cold after keeping 1 year have a better suspending power than those made by heating.

Tragacanth is often used together with acacia to insure stability of emulsions. Smith and Hazley[14] conclude acacia is a true emulsifying agent stabilizing by means of a colloidal protective film on the oil globules, but such emulsions possess low viscosities and cream rapidly. Tragacanth alone is of little value as an emulsifying agent, producing coarse emulsions the stability of which is secured by mechanical means rather than by a protective film around the oil globules, but when added to an emulsion prepared with acacia, creaming is obviated and a permanent emulsion results. Rowson states that no dehydration occurs here, probably owing to the fact that the acacia is adsorbed as a film on the oil globules and is not present in solution of the continuous phase of the emulsion.

[11] S. N. Glarum, *Am. Dyestuff Reptr.*, **26**, 124 (1937).
[12] J. M. Rowson, *Quart. J. Pharm.*, **10**, 404 (1937).
[13] N. Evers and T. McLachlan, *Pharm. J.*, **118**, 746 (1927); *Year Book Pharm.*, 634 (1924).
[14] E. L. Smith and V. Hazley, *Year Book Pharm.*, 362 (1930).

Chapter 5

Miscellaneous Gums

Gums from the Prunus Tree

Many of the cultivated trees which are of value for their fruit, yield gums which show swelling properties and form jellies more or less transparent and more or less uniform.

On the European Continent cherry gum is gathered from *Prunus avium* and *Prunus cerasus*. These are the common cherry tree. At various times in the United States marketable parcels are offered resulting from off-season collection by farmers and marketing organizations seeking by-products of their fruit distribution business. Supplies are not constant, but the gums find application in pharmaceuticals, cough sirups and "patent medicines."

The cultivated peach tree, widely grown in the states bordering the Atlantic Ocean in the United States from New York to Georgia, yields a hard reddish hydrophilic gum where the branches are bruised. The varieties of peach and plum such as *Prunus amygdalus, Prunus armeniaca, Prunus communis, Prunus eburnea,* and *Prunus mahalet,* have been studied to a small extent. Some attempts have been made to collect these materials, as in the case of the cherry gums, as byproducts of fruit packaging and marketing operations. In the case of *Prunus persica,* gum is formed on old or diseased trees as a result of the boring of various insects. Orchardists recognize this evidence as need of better pruning, elimination of dead wood and removal of sources of infection.

In India, gums are collected from the various fruit trees as well as that of the almond and plum. These enter into some of the miscellaneous and irregular East Indian gums. They often constitute a mild form of adulteration of arabic, ghatti, and tragacanth.

Syrian gum, sometimes designated as carmania, is reputed to be the exuded masses from varieties of almond and plum trees. These are often used locally in confectionery.

In studying the manner of formation of wattle gum, Greig Smith[1] claimed to have isolated two kinds of bacteria from the twigs of the tree. When these bacteria were grown on a suitable medium they produced a

[1] G. Smith, *Proc. Linn. Soc. N. S. W.*, Pt. III, Sept. 24, 1902.

slime containing araban and galactan. Bean and Edie[2] held the view that a specific organism is responsible for the formation of gums. When, however, they inoculated gum-bearing trees with this organism, decreased amounts of gums resulted. Ruhland[3] was able to isolate *Bacillus spongiosus* from diseased cherry trees which formed a gum yielding only arabinose on hydrolysis. Greig Smith[4] maintained that he discovered *Bacterium acaciae* in the gum of plum, cedar, peach, almond, and date trees. It is claimed that *Bacillus persicae* which is found on peach and almond trees also probably influences the formation of gums. In a sucrose medium it forms a mucous or gummy matter which gives galactose and arabinose on hydrolysis.

Gums from North and South America

Angico gum is produced from a medium sized tree *Piptadenia rigida* which is common in eastern Brazil. The gum is soft, dark red in color, and small commercial shipments are in the form of lumps 2 or 3 inches in diameter. It is unfortunate in connection with forest products in Brazil that to date gum and resin collection has not been coordinated with botanical knowledge, so that there are often shipments of materials which have good optical appearance but which chemically and botanically are mixtures of hydrophilic colloidal gums and true water-insoluble resins. Rangel[5] described the various species of *Piptadenia* from which Angico gum is obtained. The gum is similar to gum arabic and is used in Brazil as an adhesive and as a constituent of medicines. The methods of collection and packing are primitive so that the gums are of inferior quality.

Angelique gum is reputed to be the exudation of the large tree *Dicorynia paraensis* which is fairly common in the northern portions of South America. The gum is reddish brown to black, contains tannins, and swells slightly in water to form a jelly.

Balsam, often known as gum balsam or Canada balsam, is not a hydrophilic material but is the resinous exudation of the Canada balsam evergreen and related species of abies. The tree was first described as *Pinus balsamea Linn* and later *Abies balsamea* and *Pinus canadensis Linn,* but the most acceptable name appears to be *Abies balsamea Mill.*

Brea or beira gum is available in large quantities as thin slender stalactitic masses of exudations from the tree *Caesalpina praecox.* These small trees grow abundantly on mountain slopes in northern Argentina. Collection of the gum is carried on to supply local industries, and were

[2] Bean and Edie, 4th Report Wellcome Tropical Research Laboratories, Khartoum.
[3] Ruhland, *Ber. Deutsch. botan. Ges.,* XXIV, 393 (1906).
[4] G. Smith, *Centr. Bakt.,* Pt. II, 698-703.
[5] J. L. Rangel, *Rev. quim. ind.,* (Rio de Janeiro), **12,** 16-18; 128-30 (1943); Haya S. Schneider, *Rev. chim. ind.,* (Rio de Janeiro) **6,** 286-90 (1937).

the business systematized the material could probably find an export market. The gum is transparent, reddish in color, and shows hydrophilic qualities although often samples contain some tannins. Local uses are found in adhesives and textile operations. The gum has many additional and often unrecognized native designations.

Cactus gum is collected locally from various species of the cactus plants such as opuntia and the sagarro which is widespread in the southeastern part of the United States, Mexico, Central America, and northern South America, particularly in semi-arid districts. The gum is cream yellow to brown in color and to some extent resembles gum tragacanth, particularly in its lump form. It is hydrophilic, swelling in water and forming creamish white opalescent jelly. In Mexico it finds application in the local textile business as a size and a cloth stiffener. No recognized gradings exist and the collection is of the avocation variety rather than of the persistent business type.

Guamacho gum is from a South American variety of cactus *pereskia*. Its characteristics are similar to those of the other cactus gums.

Goma de Cedro, cedro gum or cedar gum is occasionally found and collected from the tree *Cedrela odorata* or the fragrant cedar which is employed for furniture and for cigar boxes. These trees abound in the American tropics and the West Indies. The gum is usually red to brown in color, shows hydrophilic properties, and forms clear jellies. Some use is made in mucilage in connection with cigars and packaging these, but mostly this is of local application. There is occasional use of the gum in connection with cosmetics and pharmaceuticals.

Goma de Guanacaste is a local product in tropical America and the West Indies from the trees *Enterolobium cyclocarpum* and *Enterolobium ellipticum*. The gum is usually dark in color and does not show the same degree of hydrophilic character as the gums of commerce. Its application is local, largely in pharmaceuticals of native manufacture.

Mesquite gum, also known under the locality designation of Sonora, is gathered from small thorny trees which are abundant in the arid or semi-desert regions of western Texas, New Mexico, Arizona, and north Mexico. Botanically the trees are of the prosopis family and include *Prosopis juliflora, Prosopis dulcis, Prosopis horrida, Prosopis inermis, Prosopis glandulosa, Prosopis pubescens, Prosopis spicigera*. The habitat of the tree covers the dry mountainous regions of South America as far south as Chile. Often, as a function of its random collection, the gum is dark in color, brittle and soft, being of secondary quality in comparison to gum arabic. Mesquite gum is an article of commerce in many South American districts and its applications are in general those of the hydrophilic gums. The average quality is not always entirely soluble in water, but the gums

swell and form soft jellies from the portions which are not readily soluble.

It is of interest to note that mesquite gum is the raw material for the preparation of *l*-arabinose as given in some of the standard chemical methods.[6] The gum requires about 24 hours to dissolve when 3 kilograms of mesquite gum is dissolved in 11 liters of water. The sugar is prepared by hydrolyzing the gum with sulfuric acid at 80 to 90°C., neutralizing with calcium carbonate, clarifying by the means of decolorizing carbon, filtering the solution and evaporating in vacuum. Separation of the arabinose from the non-sugar material is by alcoholic extraction.

Cherry gum,[7] peach gum,[8] Australian black wattle gum[9] are also given as sources for the material.

Mangrove gum is from the mangrove tree common in the semi-tropical and tropical regions of the American continents, *Rhizophora mangle.* The gum is largely of botanical interest, being dark red in color. It absorbs water in considerable amounts to form amber-colored jellies whose stiffness is of the same order as that of gelatin.

Mimosa gum from the flowering tree *Mimosa asperita* and related varieties is largely of chemical and botanical but not commercial interest. Small concentrations of the gum form highly viscous solutions.

The tree *Symphonia globulifera,* whose habitat is the West Indies, the northern coast of South America, and portions of Brazil, yields hydrophilic gums which find local application as thickeners for native textile work and "starch builders." Sometimes these gums are offered in small quantities as pig or animal gums, inasmuch as they are collected from trees which have been bruised by rooting rodents or other animals.

Gum rosin is the resinous exudation of the coniferous trees, the order *coniferae* with particular reference to the genus *Pinus* and the variety *Pinus maritima.* Rosin is also known as colophony and is really the distillation product of the tree exudation, the volatile portions of which are the turpentine and essential oils, and the portions remaining in the still being the rosin. Gum thus is another designation for the tree exudation which includes the turpentine and the rosin before they are separated. Gum rosin and gum thus are misnamed and are not true gums, having no water-soluble or hydrophilic characteristics but, contrariwise, are hydrophobic and only solvent soluble.

In the United States long-standing custom has continued the use of the word gum as trade names and in corporate designations, where actually the material under discussion is a resin. Some attempt at distinction

[6] "Polarimetry, Saccharimetry, and the Sugars," *Circ.* 440 National Bureau of Standards, U. S. Gov. Printing Office, 1942, pp. 457-58.
[7] H. Kiliani, *Ber.,* **19,** 3029 (1886).
[8] W. Stone, *Am. Chem. J.,* **12,** 435 (1890).
[9] T. S. Harding, *Sugar,* **24,** 656 (1922).

is made by terming the true gums dealt with in this volume the "water-soluble gums." Misnomers for the natural resins[10] as gum damar, gum copal, gum congo, gum kauri, manila gum, all of which are resinous exudations and not true gums, are prevalent. In a somewhat related manner, the so-called gum resins which are mixtures of hydrophilic and hydrophobic constituents also exist in the group of materials known as gum benzoin, gambier, catachouc, gamboge, guaiac, kino, myrrh, and the balsams of Peru, Tolu, and storax. The addition of dragon's blood completes the list of the commercially important gum resins which, although designated gums in commerce, are not hydrophilic in their nature but are much more closely related to the resins.

[10] C. L. Mantell, C. W. Kopf, J. L. Curtis, and E. M. Rogers, "The Technology of Natural Resins," John Wiley & Sons, Inc., New York, 1942.

Chapter 6

Hydrophilic Colloids from Seaweeds

Agar, Irish Moss, Algins

The masses of seaweed found along the ocean coasts are raw materials for a growing number of process industries. They have long been an intriguing object of study by the botanist and the oceanographer. For centuries seaweed has been employed as a plant fertilizer, as a food or ingredient of pharmaceuticals, or as a source of chemicals such as soda, potash, iodine, and for a time, acetone by a fermentation process. The extensive development of seaweeds as a source of hydrophilic colloids or gums under the names of agar, carrageenin, algin and the alginates, particularly in the United States, had its origin about the period of World War I.

The hydrophilic colloids or mucilaginous substances are derived from two general groups of algae; one class such as algin from the brown algae, of which the major classes are the Fucoids and the Kelps; the other, the red algae, of which the important seaweeds are the carrageens or chondrus and the agarphytes. A classification is given in Fig. 16.

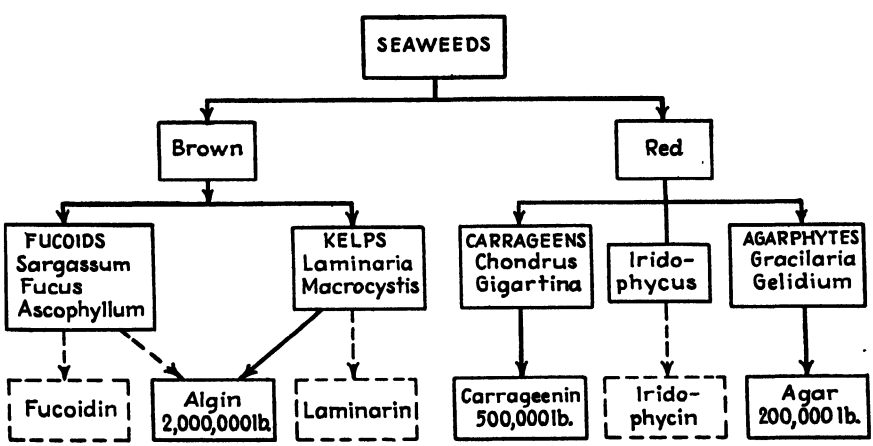


Figure 16. The seaweed colloids.

The colloids derived from the different algae have a number of similar properties but also a number which physically and chemically are divergent and make one colloid preferable to the others for specific applications.

The seaweed algae may be further classified according to their habitat into submerged plants on the one hand and rock adherers on the other, and into those which prefer strong tidal areas and those whose nutritive requirements are met in sluggish areas strong in phosphates and nitrates as in ponds, bays, and estuaries.

The submerged weeds grow in areas as deep as five fathoms,[1] while the rockweeds are found between the low and high tide levels.

Most of the masses of seaweed found on the seashores in Europe and North America are brown algae. The two principal species are *Laminariae*, a deep water type and *Fucus* of the rock kind found between tidal levels. The *Laminariae* are found in enormous amounts—for more than a century the dried weeds were burned and iodine or iodides extracted from their ashes. Lamarin was extracted and discovered in 1885. The manufacture was not satisfactorily worked out until recently so that the material has not reached the importance of algin or agar. Another kelp of the giant type, *Macrocystic pyrifera* formerly a source of potash and iodine, is now the raw material for algin and the alginates.

The fucus intertidal brown algae have to date not reached commercial importance as a raw material.

The red algae have served as foods for centuries in the Orient, and have been the subject of planned cultivation. The agarphytes, particularly the *Gelidium* (Fig. 17), have been the raw material of the Japanese agar industry for centuries. Since World War I, it has been the principal source of the American agar on the Pacific Coast while the *Gracilaria* (Fig. 18 and 19) has been the raw material for the East Coast producers.

In Europe the red algae were used for food in the form of Carrageen or Irish moss, derived from a rockweed growing between tidal zones, the *Chondrus crispus*.

Agar, algin and carrageenin are the end products of manufacture with the seaweeds as raw materials. In general, their raw materials, their gathering, their manufacture and uses are somewhat similar; they differ in detail and so are separately treated. The products are economic and technical competitors.

The seaweed *Ascophyllum nodosum* is a source material for the preparation of the rare sugar *l*-fucose or *l*-galactomethylose, which is made by fermentation under specific conditions.[2] The seaweed is treated by sulfuric acid extracts.

[1] 1 fathom = 6 feet.

[2] J. A. Widtsoe and B. Tollens, *Ber.*, 33, 132 (1900); A. Gunther and B. Tollens, *Liebigs Ann. Chem.*, 271, 86 (1892).

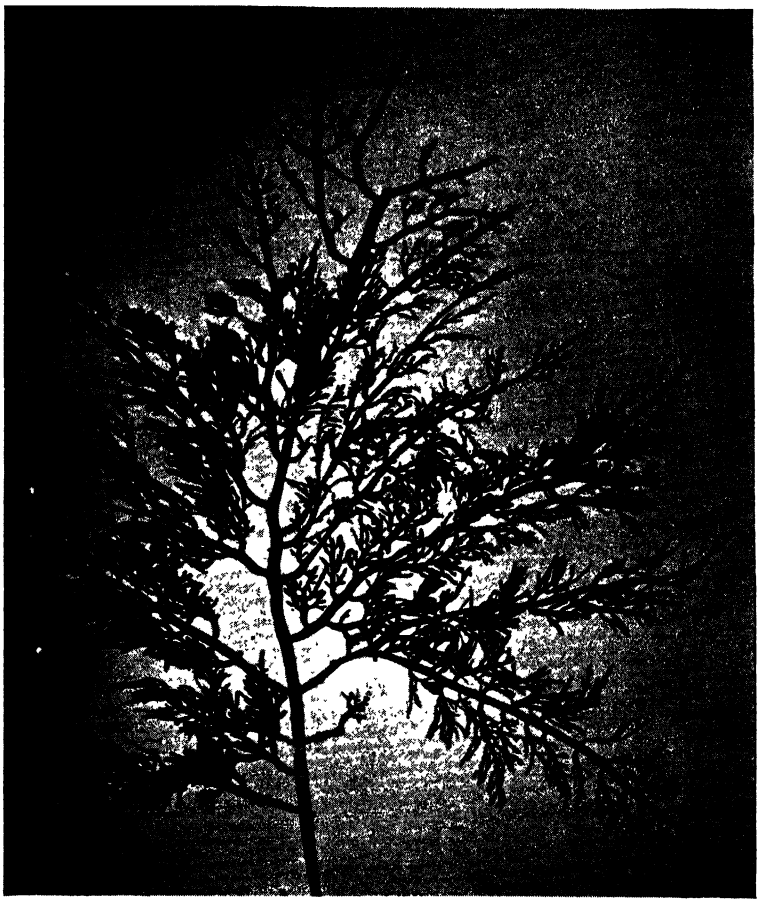


FIGURE 17. *Gelidium cartilagineum* from San Luis Obispo County, California. (*Courtesy Fish and Wildlife Service, Dept. of the Interior, Washington, D. C.*)

AGAR

The United States Pharmacopoeia defines agar as the dried mucilaginous substance extracted from species of gelidium and closely related algae, the agar containing no more than 1 per cent acid insoluble ash, and not more than 16 per cent moisture.

Agar is practically nitrogen-free and akin to carbohydrates. The seaweeds from which agar may be made are found widely scattered, e.g., on the seacoasts of Japan, China, Ceylon, Malaysia, Australia, Mexico, lower California and California. Agar is produced from *Gelidium cartilaginium, Gelidium corneum, Gelidium coulteri* and others.

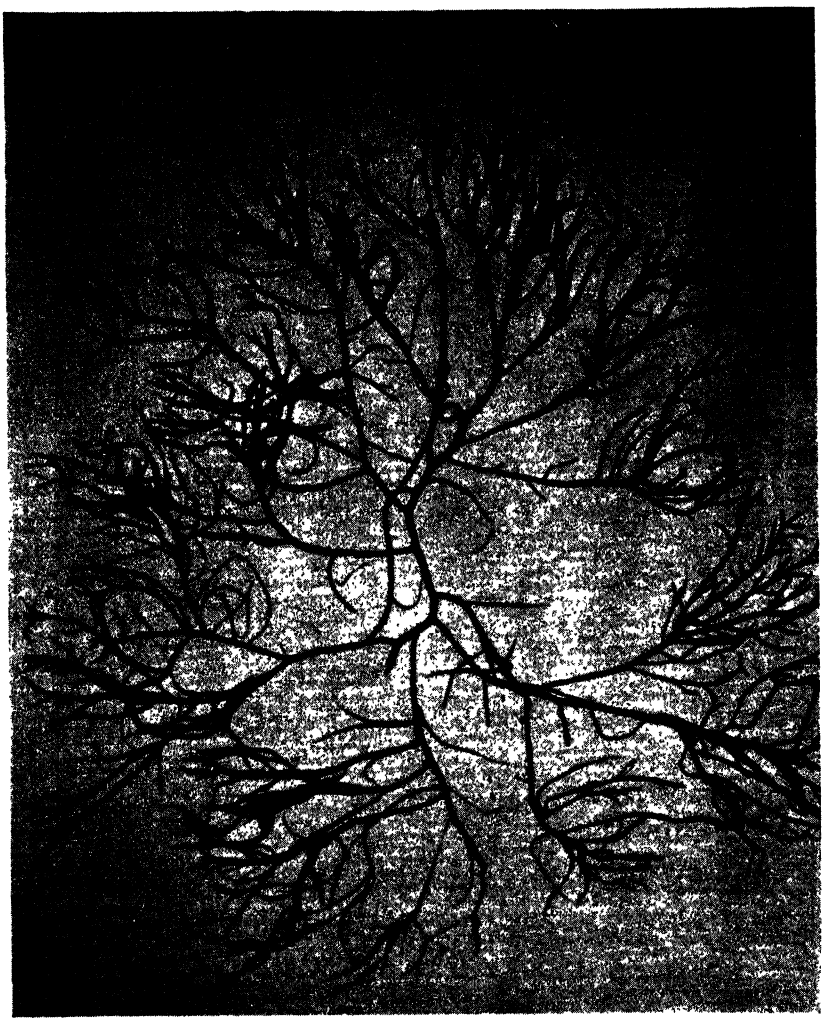


FIGURE 18. Algae (*Gracilaria confervoides*), Beaufort, N. C. (*Courtesy Fish and Wildlife Service, Dept. of the Interior, Washington, D. C.*)

Tseng[3] proposed a definition of agar as "the dried, amorphous, gelatin-like, non-nitrogenous extract from gelidium and other red algae, being the sulfuric ester of a linear galactan, insoluble in cold water, but soluble in hot water, a dilute neutral solution of which (1 to 2 per cent) sets on cooling to a firm gel solidifying at 35 to 50°C., and melting at 90 to 100°C."

Agar is a polysaccharide of complex composition. It occurs as a con-

[3] C. K. Tseng, *Sci. Monthly*, **58**, 24-32 (1944).

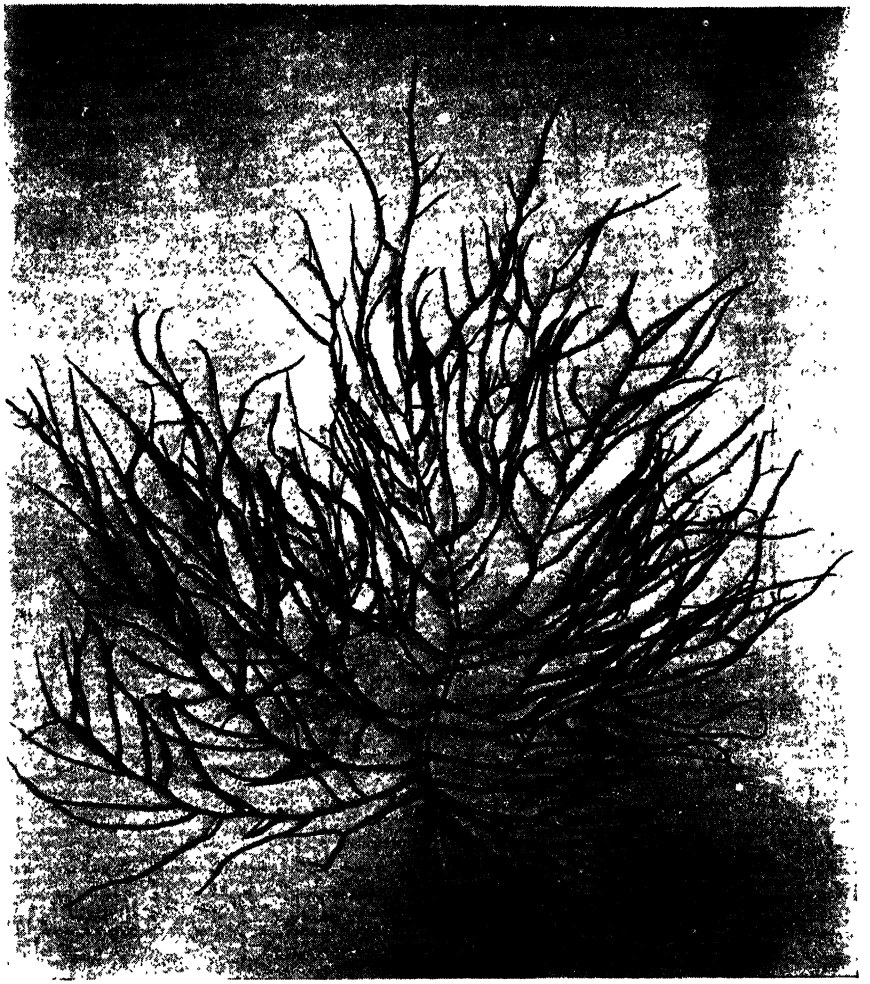


FIGURE 19. Algae (*Gracilaria confervoides*), Beaufort, N. C. (*Courtesy Fish and Wildlife Service, Dept. of the Interior, Washington, D. C.*)

stituent of the cell walls of agarphytes of which gelidium, eucheuma, and gracilaria are typical. It can be extracted by boiling the mechanically cleansed seaweeds in water, cooling the extraction to the congealing point, comminuting the gel by various means, thawing and desiccating the subdivided gel by solar or artificial heat so that a dry-to-the-touch product is made.

The United States depended on Japan primarily for its agar, though there was one domestic producer on the West Coast at San Diego, Cali-

fornia. The United States imported 500,000 to 700,000 pounds a year till 1941. American production has been irregular and output data available are incomplete. It has been as high as 118,000 pounds (in 1925) but in 1934 it was down to 2,000 pounds. Production statistics are given in Table 12.

Agar is also known under various other names such as Japanese isinglass, Chinese isinglass, vegetable isinglass, seaweed isinglass, Japanese gelatin, bar or square kanten, slender kanten and others. Production of agar from seaweed is said to date from the seventeenth century in Japan. The remnants of a species of seaweed served as a food in Fushimi, Japan, had been thrown to the ground on an extremely cold day. The fragments froze hard and the host thought it could be used as a delicacy. A priest who tasted the edible jelly expressed his delight and named it "Kanten" or literally "Frozen Heaven."

Table 12. U. S. Production of Agar and Imports from Japan*

Year	U. S. production (pounds)	Imported from Japan (pounds)
1923	7,755	.....
1924	7,281	.....
1925	117,773	.....
1926	29,877	.....
1927	.....	.....
1928	22,797	.....
1929	5,140	.....
1930	44,895	.....
1931	28,395	.....
1932	10,009	.....
1933	41,557	.....
1934	1,802	.....
1935	8,061	.....
1936	data not available	.....
1937	21,208	704,000
1938	7,170	589,000
1939	8,098	497,000
1940	24,000	635,000
1941	52,000	597,472
1942	110,054	.....
1943	165,954	.....
1944 (Jan.-Aug.)	113,762	.....

* Production output figures for 1923-1938 and first nine months of 1939 are from U. S. Tariff Commission report (1941). Production data from 1940 were supplied by present agar manufacturers. No records are available of Matsuoka's agar production from 1920-1923.

Another story is that a Japanese innkeeper, Tarozaemon Minoya, noted that some agar jellies which had been thrown outdoors and frozen during the night, had thawed during the next morning and had been dried by the

sun. The jelly had been converted into membranous, porous flakes which were translucent. The observation provided the basis for the commercial method used by Japanese manufacturers.

The grades of agar offered in the United States are the domestic products and the three Japanese products: Saghalien, Kobe and Yokohama. Saghalien quality, available commercially since 1915, comes from the Japanese part of Saghalien Island. It is not as elastic as the other Japanese grades, but coagulates better, that is, it has more strength. It is said to effect appreciable savings in sugar (as high as 20 to 30 per cent) in confections. Saghalien is imported in only small quantity and its cost is highest of the imported types. Kobe quality is divided into three grades, numbers 1, 2, and 3, the best being number 1. The standards for the different grades are set each season by the Osaka, Kyoto and Hyogo Isinglass Association which embraces all the manufacturers, large and small who manufacture the Kobe quality in the three prefectures included in the association name. Baling is done by public balers under supervision of the association and the Japanese Department of Agriculture. The Kobe quality which represents about 80 per cent of the Japanese output and a far larger proportion of the United States' import is made under better control than the Yokohama quality. It is better also in color, appearance and strength, particularly the latter. Yokohama quality also is divided into grades number 1, 2, and 3. The manufacturing district is centered around Nagano, about 75 miles from the east coast of Japan. It is shipped to Yokohama and there packed, which is why it is known as "Yokohama" although its real name is "Shinshu." Most of this quality is consumed in Japan, only 20 to 30 per cent being exported and this mainly to Europe. The domestic product is of one grade. Its appearance is not as good as the number 1 Kobe product, nor as white, but is freer of foreign matter, has no seaweed taste, has a higher jellying power and absorbs more water. The Japanese products are available generally as strands, sheets, in shredded form, blocks and powder. The American product is available as flakes and powder. Commercial agar varies from colorless to gray, yellow, pink, and even black.

The seaweed from which agar is extracted grows at the bottom of the sea. It is collected in May to October by divers who make many descents during the day, cut the weeds free and return to the surface with a bundle of them. In Japan the seaweeds ("Tengusa," "Yegonori" and "Oganori" are the chief types) are left on the beach for three or four weeks to dry and bleach and later are taken for manufacture to the mountains, for example back of Kobe where is found the right combination of cold nights and bright sunlit days to give the alternate freezing at night and the sun's thawing and bleaching action in the daytime.

The manufacturing procedure[4] involves cleaning the seaweed by beating, pounding, and washing in cold fresh water until free of salt and most of the foreign matter. It is then boiled for 30 to 40 hours to extract the glutinous matter and is allowed to settle undisturbed. Separation of grades is made by scooping off layers of the solution without stirring; the top 70 per cent usually furnishes the best grade, number 1. The solution is poured into trays to cool and set, after which the jelly is put in a press with holes in the bottom through which it is forced as strips. These are

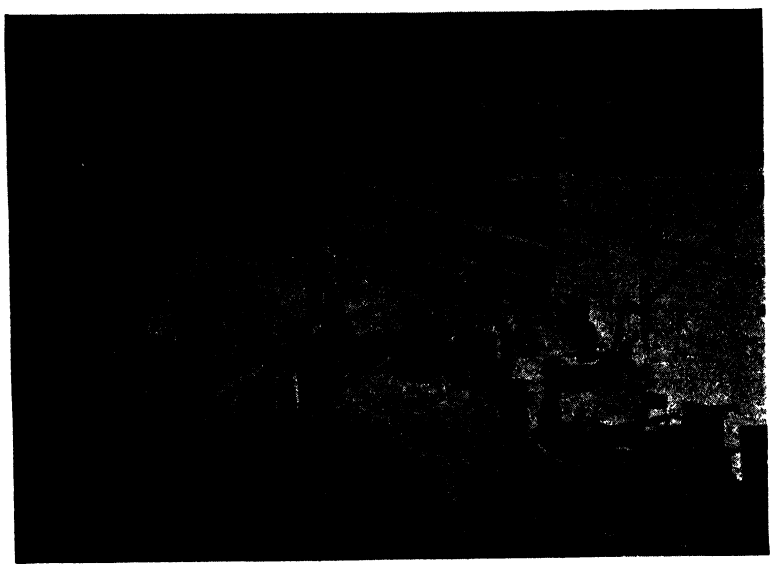


FIGURE 20. Washing the seaweed. (*Courtesy T. M. Duché & Sons, Inc.*)

laid out to dry and bleach on shelves in the open or in sheds which have a roof but are open on the sides. The dried, bleached product is sold either in strip form to the Japanese market or in chopped up or in ground form to the export trade and, before American production replaced that of the Japanese, to the United States.

Figure 20 shows the interior of a washing plant where the seaweed is beaten and washed in open tanks in fresh water. Figure 21 shows the furnace section for that portion of the plant where the seaweed is boiled to obtain the agar extract. Figures 22 and 23 show sections of the drying fields where the agar is subjected to alternate freezing and thawing in the mountain areas of Japan where this processing is done. Ordinarily the

[4] The Drug and Cosmetic Industry, July 1934, p. 21. May 1935, p. 558; D. K. Tressler "Marine Products of Commerce," Reinhold Publishing Corporation, New York (1923); information from T. M. Douché and Sons, Inc., New York.

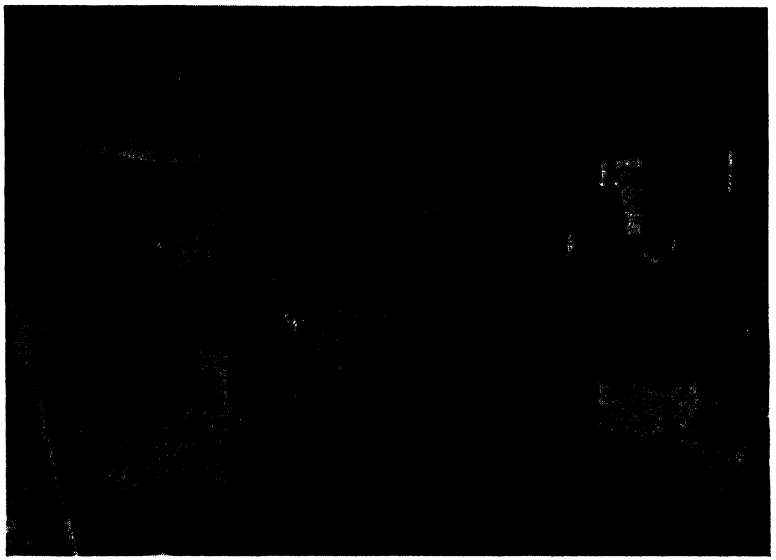


FIGURE 21. Heating plant for boiling the seaweed. (*Courtesy T. M. Duché & Sons, Inc.*)

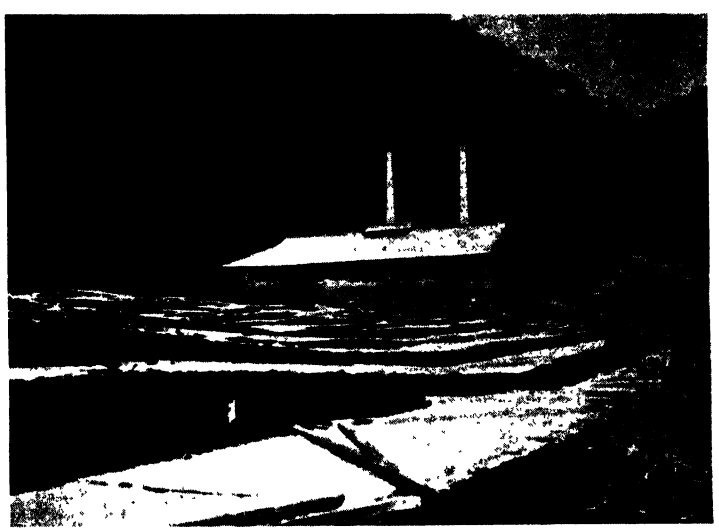


FIGURE 22. A drying field where the agar strips are spread on shelves in the open. The cold mountain air and the sun play important roles in the processing. (*Courtesy T. M. Duché & Sons, Inc.*)

operation is carried on in the open, but Fig. 24 shows an undercover drying shed with sides open to the air for some of the better grades of agar.

Matsui at the Imperial University of Tokio in 1916 reported the analyses of the three major types of seaweed used in the manufacture of

FIGURE 23. A drying field where the agar strips are spread on shelves in the open. The cold mountain air and the sunshine play important roles in the processing. (*Courtesy T. M. Duché & Sons, Inc.*)

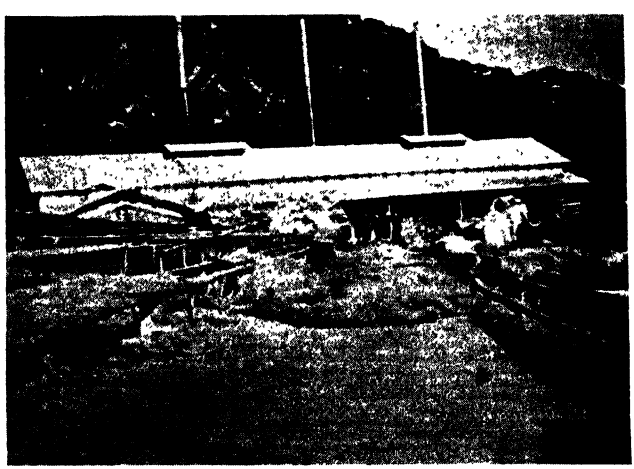


FIGURE 24. Undercover drying shed. Sides open to air. (*Courtesy T. M. Duché & Sons, Inc.*)

Japanese agar known under the names of Tengusa which are various species of Gelidium, Yegonori, and Ogonori. All the analyses are on the dried weight basis and are given in Table 13.

Table 13. Analysis of Three Kinds of Agar (Per Cent of Dried Material)

	Tengusa (Various species of Gelidium)	Yegonori	Ogonori
Ash	4.32	3.04	3.54
Lime	0.28	0.48	0.39
Magnesia	0.52	0.94	0.84
Alumina	—	0.45	0.55
Nitrogen	2.01	2.19	0.59
Crude protein	12.56	13.67	4.29
Fiber	17.89	12.25	4.32
Galactan	23.70	24.88	22.14
Pentosan	2.30	5.19	1.21
Methyl pentosan	0.93	2.13	0.97
Reducing sugars after hydrolysis with dilute acid	23.20	48.38	45.20

Table 14 shows a comparison of various grades of Japanese agar in the form of analyses through the courtesy of T. M. Douché & Sons, Inc., New York, of Saghalien, Kobe, and Yokohama agar-agar, which represent three grades normally imported into the United States. The analyses are on the agar as received, and show a water content of the order of 23 to 24 per cent. The crude protein is low, but the acidity is appreciable.

Table 14. Composition of Japanese Agar

	Water %	Acidity %	Crude Protein %	Crude Fiber %	Soluble Non-Albuminous %
As Received					
Saghalien	23.90	2.90	1.43	16.14	55.64
Kobe	23.90	2.90	1.43	16.14	55.64
Yokohama	23.12	2.47	1.50	19.27	53.64
On Dry Basis					
Saghalien	—	2.58	0.51	0.12	96.80
Kobe	—	3.82	1.88	21.19	73.12
Yokohama	—	3.21	1.96	25.06	69.78

The *d*-galactose content of Saghalien agar is contained in the soluble non-albuminous portion. Of the approximately 55.6 per cent of soluble non-albuminous material, 39.6 per cent is galactose. In the Yokohama material showing approximately 53 per cent of soluble non-albuminous, 33 per cent of this 53 is galactose.

The differences in the three qualities are illustrated in the coagulating test figures of Table 15.

Table 15. Coagulating Test*

(Made on concreted agar composed of 200 g. of water with 2 g. of agar melted therein)

	Surface g.	Middle g.	Reverse g.
Saghalien Agar	74.74	42.96	40.93
Yokohama Agar	34.96	30.99	20.38

* This analysis report is made by the chemical department of The Imperial University of Hokkaido, Japan.

American Production. By far the greater proportion of the American agar industry is located in the southern part of California.

FIGURE 25. *Gracilaria confervoides.* Gathered from 1 sq. meter, San Diego Bay, California. (*Courtesy Fish and Wildlife Service, Dept. of the Interior, Washington, D. C.*)

In 1919 Matsuoka and six other Japanese built the plant of the American Agar Co., in what is now Glendale, California. Mechanical refrigeration replaced the natural method of the Japanese procedure and chlorine bleaching replaced that of the sun's rays. The raw material was *Gelidium cartilagineum* from the San Pedro breakwater. Some of the operating details are given in United States patents.[5] Uneconomic operation, as a result of too much hand labor, resulted in commercial failure.

[5] C. Matsuoka, U. S. Patents 1,399,359 (1921); 1,453,848 (1923).

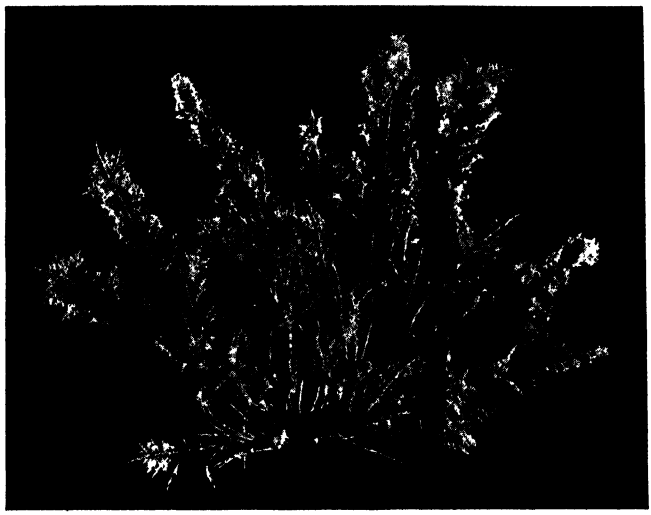


FIGURE 26. *Gelidium cartilagineum.* Living plant, La Jolla, California. (*Courtesy Fish and Wildlife Service, Dept. of the Interior, Washington, D. C.*)

FIGURE 27. *Gelidium cartilagineum.* Young tetrasporic plant, La Jolla, California. (*Courtesy Fish and Wildlife Service, Dept. of the Interior, Washington, D. C.*)

John Becker reorganized the plant in 1923 and mechanized the process.[6]

The American production from 1923 to 1926 came from Becker's plant. The operation terminated in 1933. In the same year S. F. Corfield started the United States Agar Co. in National City, California, but Japanese agar fell to an average price of 49 cents per pound and in 1934 large consignments of Kobe No. 1 sold at 40 cents. The plant of the United States

FIGURE 28. *Gelidium cartiligineum.* Young tetrasporic plant, La Jolla, California. (*Courtesy Fish and Wildlife Service, Dept. of the Interior, Washington, D. C.*)

Agar Co. reprocessed Japanese agar. The United States Agar became a part of American Agar and Chemical Co., at San Diego, working on gelidium from Mexico, Laguna, San Pedro and Redondo, in southern California.

In 1942 the Agar Products Co. of Los Angeles, California, lost their

[6] John Becker, U. S. Patent 1,701,744 (1929) for Combined Congealer and Sizer; U. S. Patent 1,703,654 (1929) for Dehydrator and Flaker; U. S. Patent 1,712,785 (1929) for Agar Product and Process; U. S. Patent 1,726,942 (1929) for Dewaterer for Flaked Agar.

source of crude imported agar from Japan. They turned to the nearby regions of the Pacific Ocean for their raw material. The Pacific Agar Co., at Whittier, California, began operations in 1943. Increasing demand for agar caused two factories in Mexico to come into operation.

Humm[7] investigated the agarphyte, *Gracilaria confervoides* shown in Fig. 25. Commercial quantities are present in the region of Beaufort, North Carolina. Agar from gracilaria will serve most uses, but agar from gelidium is reputed to be better for bacteriological cultures. Some eastern

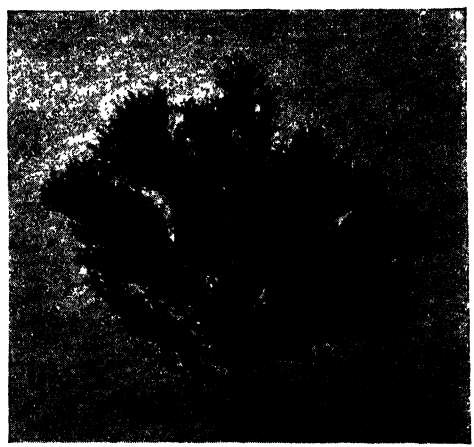


FIGURE 29. *Gelidium nudifrons.* Tetrasporic plant, Laguna, California. (*Courtesy Fish and Wildlife Service, Dept. of the Interior, Washington, D. C.*)

plants using gracilaria came into existence at Beaufort, North Carolina, Scituate, Massachusetts, and New York.

Manufacturing Process. The true agarweed, the *Gelidium cartilagineum,* is found in quantities which are commercially harvestable only in southern California and the Baja California district of Mexico, between Point Conception in the north and Magdalena Bay in the south. The plant and its type of growth are shown in Figs. 25, 26, 27 and 28. The plant grows from a foot and a half to four feet tall and prefers the edges of rocks in the path of strong tidal currents. Other species sometimes used are, *Gelidium nudifrons* shown in Fig. 29 and *arborescens.* These are the "hair agar" in that they have thin hair-like filaments. These plants prefer deep water and have a bush-like growth about three feet in height. They must be harvested by divers. The *Gracilaria confervoides* is the source of agar in the Eastern States. This plant prefers sheltered bays where the movement of water is sluggish. Harvesting is by raking at high tide and hand picking at low tide. One ton of sun-dried agarphyte re-

[7] H. J. Humm, *Science,* N.S., **96** (2488), 230-231 (1942).

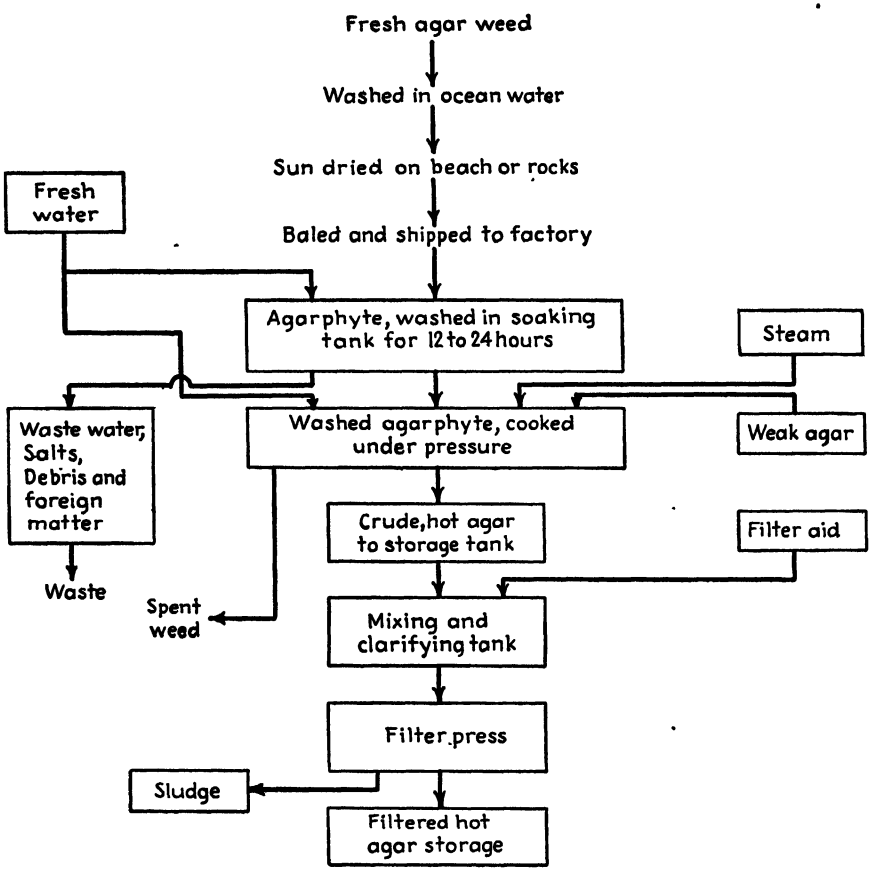


FIGURE 30. Flowsheet of agar manufacture—Part 1. Seaweed to purified solution.

quires seven tons of fresh gracilaria, but only three tons of fresh gelidium.

The flow sheet of agar production is shown in Figs. 30, 31 and 32. Figure 30 carries the manufacture to the purified solution stage, Fig. 31 to the bleached agar flakes, and Fig. 32 through grading.

The sun-dried agarphyte is soaked in water and washed with about a gallon of fresh water per pound of dried weed. Transference is made to pressure cookers, heated by 15 lb. steam where the agarphyte is digested. The first extraction is a six-hour operation in a dilute agar solution which resulted from the third of three extractions of a previous lot of material. The extract is sent on to storage while the agarphyte in the cooker is digested a second time with fresh water to give an extract going to storage. A third digestion gives a weak extract which serves as the extractant for fresh material.

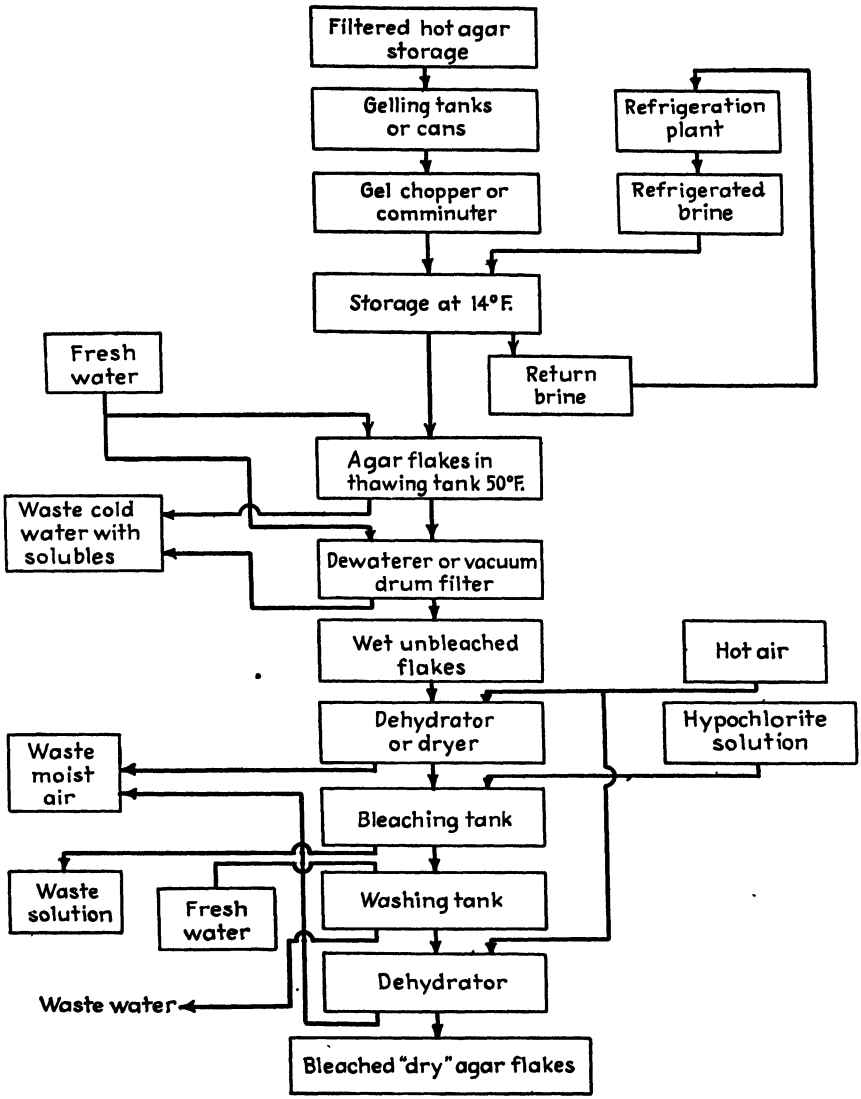


FIGURE 31. Flowsheet of agar manufacture—Part 2. Purified solution to bleached flakes.

The crude hot agar in the storage tanks is clarified by settling and filter aid introduced before passage through plate and frame presses. The filtered agar solution is transferred to tubs or cans where it gels after cooling to room temperature. The gel is chopped or comminuted and dropped into cans such as those used for artificial ice. The cans are sent to freezers

where the gel is kept at about 14°F. for two days or so. After removal from storage, the gel is thawed at about 50°F., after which it is dewatered on a rotary vacuum filter. Spray wash water on the filter removes impurities which are soluble.

The filter product goes to hot-air dryers (215°F.) of the tray or stack type and remains there until reduced to approximately 35 per cent moisture. The agar is now in the form of light flakes which are carried up the stack by the hot air and discharged into the downpipe. The downpipe drops the flakes into a tank containing 1 per cent sodium hypochlorite where the flakes are bleached. After bleaching, the excess hypochlorite content of the flakes is removed by treatment with sodium sulfite. An-

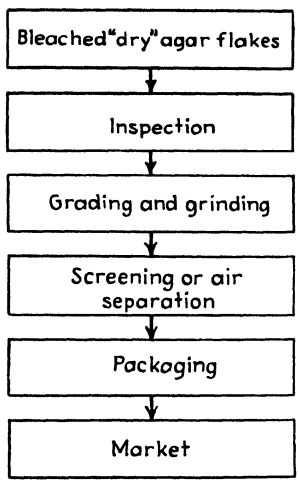


FIGURE 32. Flowsheet of agar manufacture—Part 3. Inspection and grading for market.

other washing of the flakes with fresh water follows and the wet flakes pass to a dehydrator for reduction to 20 per cent moisture content.

Often the specifications for some food products or culture media call for a sieved or graded product. Agar for these fields may be pulverized in air-swept swing hammers or other grinders with cyclone separators. A typical product shows 35 per cent through a 100 mesh and all the product through a 60-mesh Tyler screen.

Harvey[8] purified agar from diatoms and other impurities as follows: One hundred grams of fine-cut agar is added to 3000 cc. of cold 0.5 per cent acetic acid solution and allowed to stand 30 minutes. The supernatant liquid is poured off and a fresh quantity of the acid solution added. After 30 minutes this is poured off and then the swollen agar is soaked in six changes of distilled water during 12 hours. The free agar

[8] E. H. Harvey, *Am. J. Pharm.*, 97, 66 (1925).

acid may be obtained from the above by heating in 3000 cc. of water and electrodialyzing hot.[9] The upper clear layer is siphoned off and centrifuged while hot in a continuous-flow type centrifuge. The effluent upon cooling sets to a jelly which may be sliced and dried.

Agar is the calcium salt of a sulfuric ester of a colloidal carbohydrate complex.[10] The formula may be written as $R \cdot O \cdot SO_2 \cdot OH$ where *R* is the carbohydrate complex. The purified agar would then be represented by the formula $(R \cdot O \cdot SO_2 \cdot O)_2Ca$. The nature of the carbohydrate is not yet known. Although frequently referred to as a galactan, this has been seriously questioned by Lüdtke[11] who points out that galactose does not constitute more than one-third of the total carbohydrate matter.

A 1 per cent solution of the free agar acid has a pH value of 2.48 and is about 58 per cent ionized. A 5 per cent solution does not jellify upon cooling, but sets immediately upon neutralization with any base including aniline or alkaloids.[12]

A good grade of commercial agar, on the other hand, forms a jelly with as little as 1 part in 500 parts of water. If this jelly is frozen the gel structure is destroyed. Upon thawing the shreds of agar which have lain between the ice crystals will absorb about four times their weight of water. If the temperature is kept low, however, no water is absorbed. The swollen particles do not stick to each other even upon being packed or squeezed tightly. Reheating restores the jellying structure.

The swelling of agar in water is a slow process and is greatly influenced by its previous history. The slow rate of swelling of agar in water at 20°C.[13] is demonstrated by the curve, Fig. 33. If in the purification, the agar sol is kept hot for prolonged periods, the final dried product swells less. Prolonged storage of dry agar also reduces its swelling capacity. Clarke[14] found a dried agar which swelled to 3000 per cent in distilled water; after standing in the dried state for three years it swelled to only 1000 per cent. In attempting to explain this "ageing" effect, Clarke found that agar could be "aged," that is, its swelling could be greatly reduced by simply placing agar plates in an oven at 70° for two days or in a desiccator over sulfuric acid for a somewhat longer period. Of interest is a group of experiments carried out by Clarke upon the effect of desiccation of a 2.5 per cent agar gel. By means of a cork borer, two disks were taken,

[9] E. H. Harvey, *ibid.*; W. F. Hoffman and R. A. Gortner, *J. Biol. Chem.*, **65**, 371 (1925).

[10] Samec and Isajevic, *Compt. rend.*, **173**, 1474 (1921); *Kolloid Chem. Beihefte*, **16**, 285 (1922); F. Fairbrother and H. Mastin, *J. Chem. Soc.*, **123**, 1412 (1923); W. F. Hoffman and R. A. Gortner. *J. Biol. Chem.*, **65**, 371 (1925).

[11] M. Lüdtke, *Biochem. Z.*, **212**, 419 (1929).

[12] H. de Waele, *Ann. physiol. physicochim. biol.*, **5**, 877-80 (1929).

[13] F. Fairbrother and H. Mastin, *J. Chem. Soc.*, **123**, 1412 (1923).

[14] B. L. Clarke, *J. Am. Chem. Soc.*, **47**, 1954 (1925).

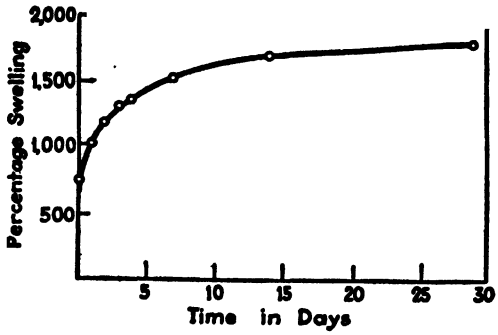


FIGURE 33. Rate of swelling of agar in water at 20°C.

one analyzed for its water content and the other placed in 35 cc. of water at 15°C., until swelling equilibrium was reached (usually in about ten days). The original gel was progressively desiccated in a current of air, then in an oven at 70°C., and finally in a desiccator over phosphorus pentoxide, disks in duplicate being removed at different time intervals and analyzed and subjected to swelling. In this manner, disks of varying water content and their swelling capacity were studied. The results are plotted in Fig. 34. By "percentage swelling" is meant the per cent increase in weight due to water absorbed in reaching the swelling capacity for each disk containing the amount of water indicated. As the agar was desiccated, that is, in going from right to left in the curve, the swelling capacity increased slowly up to point C, then very rapidly to a maximum, B, and then fell off fairly sharply. Clarke reports that his agar gels were opaque when freshly cast and that, upon drying to thin plates, the

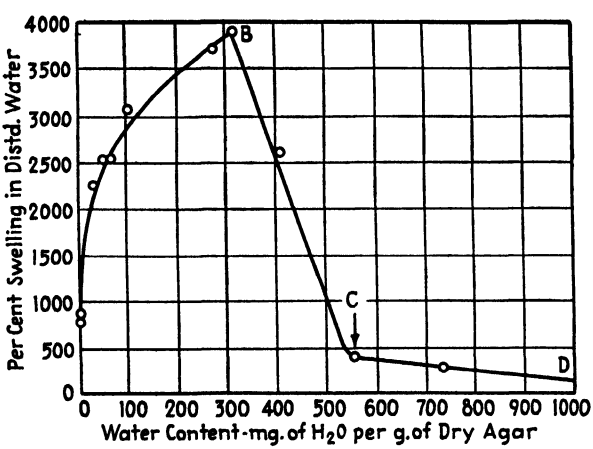


FIGURE 34. Influence of degree of drying of agar jelly upon subsequent swelling in water at 15° C.

dried disks corresponding to point C in his curve changed rather sharply to perfect transparency.

Clarke states that in the light of modern theories of gel structure it is probable that some structural alteration accompanies the drying out. This change may be in the direction of agglomeration of particles to reduce the specific absorbent surface. Since the decrease in swelling which develops slowly at ordinary temperatures and under normal pressures of aqueous vapor ("natural ageing") may be enormously accelerated at high temperatures and under low vapor pressures ("artificial ageing"), it seems necessary to assume that the structural change follows and is a consequence of the loss of water.

The effect of pH on the swelling of agar at 20°C. is shown in Fig. 35.[15]

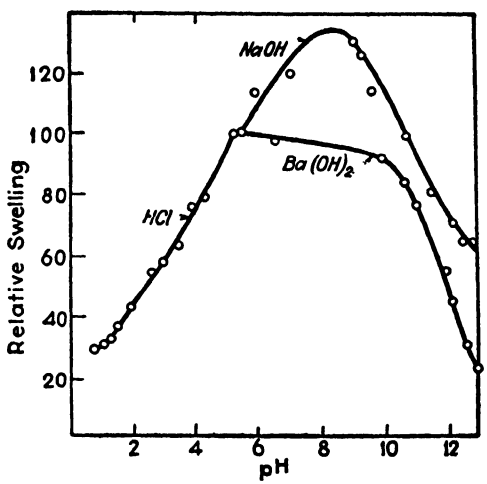


FIGURE 35. Swelling of agar at 20° C. as a function of pH.

The term "relative swelling" means the amount of solution relative to that taken up in distilled water, which is considered as 100. The swellings in hydrochloric, sulfuric, phosphoric, acetic and oxalic acids were the same when plotted as a function of pH. The swellings in ammonium hydroxide were greater than in sodium hydroxide, but the maximum in both cases was at the same pH. Fairbrother and Mastin believe that the effect of added acid is to produce a reversible equilibrium of the type:

$$(R\cdot O\cdot SO_2\cdot O)_2Ca + 2HCl \rightleftharpoons 2R\cdot O\cdot SO_2\cdot OH + CaCl_2$$

the free acid swelling less in water than the calcium salt and its ionization and swelling being further diminished by the presence of acid. The agar acid does not have jellying power and forms a viscous liquid with water.

[15] F. Fairbrother and H. Mastin, *J. Chem. Soc.*, **123**, 1412 (1923).

The swelling behavior of agar is of importance in one of its principal uses, that is in the treatment of constipation. Apparently the agar passes through the acid environment of the stomach long before an appreciable amount is hydrolyzed and in the alkaline fluids of the intestines is not hydrolyzed at all. In the alimentary canal it swells greatly but is not digested. It furnishes a large bulk of fecal matter and stimulates intestinal action without chemical irritation.

The first firm in the United States marketing a medicated agar was the Reinschild Chemical Company, New York City. Their preparations are numerous and but a few were (1) plain cut agar, (2) agar and phenolpthalein, (3) agar and rhubarb, (4) agar and cascara-sagrada.

Mineral oil has always held a leading position for the correction of constipation. The average user, however, complains of its nauseating effect, griping and leakage. Mineral oil emulsions have been developed which contain a maximum amount of agar.

Tseng[16] has estimated the distribution of agar in the United States as given in Table 16.

Table 16. Annual Agar Utilization

(*Estimated*)

	Pounds
For laxatives	100,000
Microbiological and culture media	100,000
Bakery industry	100,000
Confectionery industry	100,000
Dental impression molds	75,000
Meat packing	50,000
Emulsifiers	50,000
Cosmetics	25,000
Miscellaneous uses	50,000
Total	650,000

Agar is a non-nutritive food,[17] but is employed in food manufacture where bulk is desirable or where a hydrophilic colloid is useful for its suspending, stabilizing, thickening, or gelling characteristics.

Agar serves to increase bulk in bakery products and is useful for low-calorie breads or biscuits for reduction diets for obesity or for non-starch breads for diabetics.

In dairy products, sherbets, water ices and frozen confections, agar (but also the gums and the hemicelluloses such as locust bean) serves as a stabilizer. Agar acts more quickly than gelatin but has a low whipping

[16] C. K. Tseng, *Food Industries* (March 1945).

[17] H. W. Nilson, and J. W. Schaller, "Nutritive Value of Agar and Irish Moss," *Food Research*, 6, 461-9 (1941); T. Saiki, *J. Biol. Chem.*, 2, 251-265 (1906).

point, in which respect it is not as good as the natural gums. Agar is not recommended as a stabilizer for ice cream.

Dahlberg[18] in his study of the manufacture of water ices and sherbets recommended 0.2 per cent agar with 0.4 per cent gum tragacanth for ices and 0.2 per cent for sherbets.

Dahlberg[19] suggested agar as an ingredient in a method of manufacture of Neufchatel type cream cheese to reduce the tendency of the cheese to exude when warm and to give a firmer body which sliced in a better manner. Quantities of 0.2 to 0.1 per cent on the weight of cheese are suggested.

Agar is useful as a stabilizer in malted milk, acidophilus milk and the like.[20]

When agar was introduced to Continental Europe and the American Continent, it was offered as a replacement for animal gelatin for fruit and other jellies. Its gelling strength is about eight times that of an average gelatin and it sets at room temperature without the refrigeration requirement of gelatin. It may therefore be used in tropical countries. Compared to pectin, agar does not require sugar to make jelly.

Jelly candies and marshmallows employ ¾ to 1 per cent of the mix as agar. Icings and custard-like preparations of many varieties depend on agar for their properties.

For the softer types of meat and fish, agar is a valuable thickening and gelling agent for the food packer. The gelling properties of agar are retained to a greater extent than those of gelatin when the high temperatures and pressures of food processing are met.

Many dehydrated products of fish, soups, flavorings, and gelled concentrates employing agar have been proposed. Many were attempts to introduce Oriental dishes into the Occident, but they did not appeal to the American palate.

Probably the major non-competitive use of agar has been in the nutrient broth and culture media of the biologist. It is estimated that about one-sixth of the production is consumed in this application.

Irish Moss

Irish moss, also called carrageen, carragheen, carrageen moss, carragheen moss, pearl moss, rocksalt moss, killeen, pigwrack, and a number of other names, is the dried, sunbleached seaweed *Chondrus crispus,* found along the coasts of the British Isles, Northern Europe, New England, and Nova Scotia. The gelatinous material extracted from the seaweed by boiling water is used in the manufacture of pharmaceuticals, cosmetic

[18] A. C. Dahlberg, *N. Y. Agr. Exp. Sta., Bull. No.* 536 (1926).
[19] A. C. Dahlberg, *J. Dairy Sci.,* 10, 106-116 (1927).
[20] C. E. North, U. S. Patents 1,509,082 and 1,509,083 (1924).

soaps, paint, boiler water compounds, in non-settling chocolate drinks (probably the largest use), and in the brewing, textile, leather, and other industries.

Chondrus crispus is one of the perennial algae which is widespread in its distribution and commonly found on seashores which are rocky and broken. The fronds or leaves are densely tufted. They vary from 2 to 10 inches in height, being narrow and semi-cylindrical at the base but the stems become flat. Forking and multiple branches are typical, while the widths of the fronds vary widely. In its natural habitat in the seawater, the plants show various shades of purple or dark greenish with purple tints. This color may change as a function of the location, in that in shallow pools adjacent to the areas of high water, the *chondrus* may be olive drab, yellow, or pale green. When dry, the plants are somewhat stiff, the leaves are flexible but tend to assume a horny appearance.

As collected, the chondrus contains about 80 per cent of water. Field[21] gives the analysis of the dried or water-free substance as containing 65 per cent of gelatinous matter, 2 to 3 per cent of nitrogen in the form of nitrogen compounds, 0.7 to 1 per cent of materials grouped under the name of lipoids, and 10 to 15 per cent ash. The ash contains compounds of calcium, sodium, potassium, magnesium, chlorine, bromine, iodine, and sulfur.

Although no data as to the magnitude of world production and consumption are available, Ausman[22] states that trade sources suggest that United States consumption may range from 800 to 1,200 tons per year. Production on the New England coast is particularly important. The value of the crop in Massachusetts in 1941 was in excess of $100,000, although from year to year the production varies widely and there is no constant trend. The amount gathered seems to depend upon the inclination of local fishermen to engage in the business, and in some seasons it is large, in others it is small. Severe storms along the coast affect the crop. At times the storms tear large quantities from the rocks, scattering them widespread over long stretches of beach.

Harvesting season is from May to September. The mosser goes out in his dory and collects during the ebb tide from the dory for about four hours. A good mosser will collect about 400 pounds in this period. He uses a rake which is 12 to 15 in. across and has from 24 to 28 teeth 6 in. long with a spacing of ⅛ in. between the teeth. The rakes have handles from 15 to 20 ft. long. A small portion of the crop is gathered by hand. At very low ebb, the mosser can get at the rocks near shore and practically strip them of moss by hand, a practice that is not harmful since the rocks

[21] U. S. Bureau of Fisheries, *Econ. Circ.* No. 51 (1921).

[22] "Market for Irish Moss in the Eastern United States," Commercial Intelligence Journal, Department of Trade and Commerce (Canada), 67, No. 2010, Aug. 8, 1942 and No. 2023, Nov. 7, 1942.

become completely covered again within a few months. Moss gathered in this way yields a high price for food and drug purposes; that gathered for paint and most other uses lies from 1 to 14 ft. below ebb tide.[23]

The older process of cleaning, bleaching and drying, still used in most places, was to spread the moss in thin layers on the sand with occasional washings in hand tubs. The long weathering and bleaching turns the moss from a deep purple through wine red to straw color.

The curtailment of imports and the increased demands brought on by World War II have stimulated use of machinery for processing the moss, thereby cutting the bleaching time to a few days. One of the Massachusetts beaches is equipped with a big tank and two motors, one of which continuously pumps water from the ocean and sprays the moss while the other operates giant paddles that beat the moss. From the tank or vat the moss descends to a picking table of steel mesh; it then runs on an endless belt where periwinkles, crabs, fleas and rock eels are removed.

Irish moss may be divided into beach or storm moss and raked or pulled moss, the former being the moss that is washed up on the beaches after storms especially in the Fall and to very early in the Spring, the latter being gathered from the rocks as already described. The greatest demand is for fully bleached moss. Sunbleached material is greatly preferred; that bleached chemically with sulfur dioxide or other agents must be so designated on the bales. Care must be exercised in sun bleaching not to permit the moss to remain too wet through the night since even fog or mist will tend to destroy its gelatinizing power.

Irish moss reaches the market in bales of 100, 150, and 200 pounds from the best organized sources but in irregular packages of various sizes. Its imports into the United States are free from tariff. The grades are natural, U.S.P., and bleached.

McCance, Widdowson and Shackleton[24] give the following composition of a sample of dried Irish moss.

Water, g. per 100 g.	13.9
Unavailable carbohydrate (roughage), g. per 100 g.	71.3
Titratable acidity, cc. 0.1 N alkali per 100 g.	8
Reducing sugar, g. per 100 g.	0.0
Sucrose, g. per 100 g.	0.4
Starch, as glucose	0.0
Total available carbohydrate, per 100 g., as glucose	0.4
Total nitrogen, g. per 100 g.	1.08
Protein, g. per 100 g.	6.8

[23] M. J. Fraser, Through Ausman, *loc. cit.*

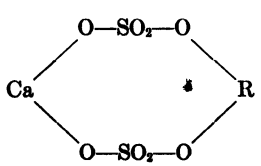
[24] R. A. McCance, E. M. Widdowson and L. Shackleton, Med. Research Council, Special Rep. Ser., No. 213 (1936).

Of the raked or pulled moss there are three broad grades generally used by the trade, (1) black or unbleached, (2) semi or half-bleached and (3) fully bleached. However, foreign matter present, amount of moisture, degree of mold and penetration, color and other characteristics vary somewhat and there are many gradations of quality. Consequently in nearly all cases the moss is sold on the basis of sample submitted. Freedom from foreign vegetation, sand, shells, decayed sea life and the like are important. One hundred pounds of wet moss is reduced to approximately twenty pounds when dry. Buyers demand low moisture content, many insisting on 10 per cent or less, and at one time some French moss was guaranteed as containing 2 per cent or less. Irish moss is sold in leaf form in various degrees of fineness. A good product for food and pharmaceutical use may be tasteless and odorless, though much of the Irish moss sold has a seaweed-like odor and mucilaginous saline taste.

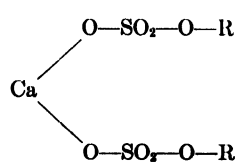
It appears that there is a relationship between the salt content of Irish moss and its gelatinizing or thickening power. If the moss be washed in fresh water and the soluble salts extracted, a solution of the washed moss does not readily gel when the temperature is lowered. In the case, however, of unbleached moss which is rinsed only in seawater and quickly dried, the extract prepared by boiling the moss in fresh water, even in concentrations of the order of as little as 2 per cent, allows the formation of stiff gels.

Chemical Constitution. Irish moss is not a single chemical compound. It is rather a mixture of a number of substances about 70 to 75 per cent of it probably predominantly the calcium salt of a sulfuric ester of a colloidal carbohydrate complex, such as I. or II. below, and containing a high proportion of galactose groups, represented by R in the formulae.

I.



II.

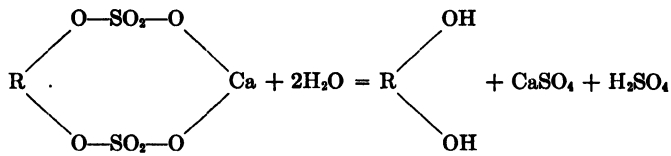


Haas[25] extracted the mucilaginous substance from Irish moss with water and reported it as represented in Formula I above.

Haas and Russell-Wells[26] found that mild hydrolysis of carrageen does not give rise to free sugars, but two ethereal sulfates are produced which can be separated by dialysis. Glucose is present in carrageen mucilage.

[25] Paul Haas, *Biochem. J.*, 15, 469 (1921).
[26] Paul Haas and Barbara Russell-Wells, *Biochem. J.*, 23, 425-29 (1929).

An aqueous solution of Irish moss shows the presence of calcium ions which can be precipitated quantitatively but sulfate ions are not present. After hydrolysis, however, the latter ions appear in solution due to the decomposition of the ethereal sulfate. Haas suggests the hydrolysis as taking place in the following manner:



Hot water[27] extracted 70 to 75 per cent soluble matter while cold water extracted only 47 per cent. Both extracts dried to similar-looking transparent, friable scales which became soft and pliable upon reaching equilibrium with atmospheric moisture and considerably swelled in cold water. The dried cold water extract dissolved completely in cold water to give a gummy solution, but the dried hot water extract dissolved only to a slight extent in cold water. On warming, however, it did dissolve to form a thin jelly when the concentration was 2 per cent and a stiff jelly when the concentration was raised to 3 to 5 per cent. Haas found other differences between the hot water and cold water extracts. Only the former is precipitated by half saturation with sodium chloride or magnesium sulfate, though both are precipitated by half saturation with ammonium sulfate. A dilute solution of the hot water extract yields a gelatinous precipitate with Rochelle salt, but on boiling the precipitate dissolves, and when the solution is cooled, a stiff jelly is obtained. The cold water extract does not behave in a similar manner. Very stable cod-liver oil emulsions could be made with the hot water extract but not with the cold water extract.

Dillon and O'Colla[28] found that by acetolysis of the mucilage of carrageen moss, two polymeric carbohydrates were obtained. One was soluble in cold water and the other soluble in hot water. The latter gave a characteristic color with iodine. Both appear to be galactans.

Russell-Wells[29] found that the cold water-extracted material contained a polysaccharide with more sodium and potassium and less calcium than that obtained by the hot water extraction. Both extracts also contained ammonium ethereal sulfates and un-ionized magnesium. She also reported that replacement of the calcium ion by ammonium ion does not destroy the gelatinizing properties of the hot extract.

Field[30] proposed that Irish moss be prepared as an article of commerce

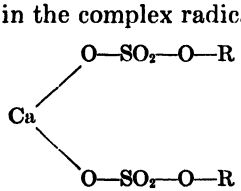
[27] P. Haas, *loc. cit.*
[28] T. Dillon and P. O'Colla, *Nature*, **145**, 749 (1940).
[29] B. Russell-Wells, *Biochem. J.*, **16**, 579 (1922).
[30] U. S. Bureau of Fisheries, *Econ. Circ.* No. 51 (1921).

by extracting the hydrophilic colloid from the moss by boiling in water and evaporating the filtered and purified solution to dryness in a vacuum evaporator or a vacuum drier. This method would eliminate the disadvantage of Irish moss as compared to agar, algin, or the natural gums, in that ordinary solutions of Irish moss require 3 to 5 hours of preparation in making the extract with boiling water. The other hydrophilic colloids may be readily put into the sol or gel form.

Haas[31] and Russell-Wells[32] and Butler[33] have shown that the ionizable calcium ion may be replaced by other inorganic ions.

Butler[34] extracted the polysaccharide complex from *Chondrus crispus*. The plants were washed with water, extracted with boiling water, filtered, the filtrate concentrated and poured into an excess of ethyl alcohol. The precipitate is further washed with ethyl alcohol and with ethyl ether. The product is soluble in hot and cold water, forming a firm gel in 2 per cent solution. The ash content of the polysaccharide is 20 per cent of its dry weight. The material extracted by water is apparently a mixture of several substances. It contains a mixture of sulfates. Butler has prepared the potassium, calcium and ammonium salts of the ethereal sulfates.

Harwood[35] points out that the calculated molecular weight of Irish moss is about 1,000 but the colloidal behavior indicates a much higher complexity. It is quite remarkable that a 1.5 per cent solution though very highly viscous was found to be 50 per cent ionized. Harwood postulates that the formula would suggest that in solution there would be pronounced ionization producing ionic micelles. Electrical conductivity confirmed this view and conductivity at infinite dilution is of the same order as that of calcium. Hence the colloid ion must possess a mobility very similar to that of the sulfate ion. From Donnan equilibrium it appears that Irish moss is a calcium salt of an organic acid in which the sulfate group is contained in the complex radical, possibly represented by



However, whether this or the originally recommended formula of Haas is correct, it seems fairly well established that both hot and cold water extracts are ethereal sulfates.[36]

[31] P. Haas, *loc. cit.*
[32] B. Russell-Wells, *loc. cit.*
[33] M. R. Butler, *Biochem. J.*, **28**, 759 (1934).
[34] M. R. Butler, *Biochem. J.*, **28**, 759-69 (1934).
[35] Harwood, *J. Chem. Soc.*, **123**, 2254 (1923).
[36] M. R. Butler, *loc. cit.*

Regarding the organic part of the chemical structure there is much still unknown. Buchanan, Percival, and Percival[37] point out that galactose residues constitute at least 31 per cent of the cold water extract and 33 per cent of the hot extract. They postulate that the galactose residues of the Irish moss polysaccharide are joined by positions 1 and 3 (as in agar, galactogen, and gum arabic) and carry the sulfuric ester group on C 4.

Butler[38] reported that decomposition of *Chondrus crispus*, as measured by oxygen consumption, has been shown to be more readily accomplished on storing in seawater than that of its polysaccharide extract. This has been attributed to the higher nitrogen content of the former. Inorganic nitrogen added to the polysaccharide extract of chondrus increased its decomposition. Samples of the extract containing different quantities of nitrogen have been found to decompose in direct proportion to the amount of nitrogen which they contain.

Gels can be prepared by soaking the moss in water and warming to 60°C. On cooling, concentrations as low as 1 per cent give a gel. The melting point of a 3 per cent gel is 27 to 30°C., that of a 5 per cent gel 40 to 41°C. The gelatinizing power is retained even after long boiling; for example, a 3 per cent solution after 3½ hr. reflux boiling sets on cooling.[39]

On the other hand, Haas and Russell-Wells[40] report that heating with acid rapidly causes loss of gelatinizing power.

Gutbier and Huber[41] reduced the ash content of a 0.56 per cent Irish moss solution by hydrolysis for 22 days to 0.02 per cent. The resulting solutions were stable to microbiological action but ageing decreased the viscosity. A 0.55 per cent mucilage kept at 25°C. gave the following viscosity values relative to water.

Age in Days	Viscosity
0	15.29
1	14.87
2	14.11
5	10.52
15	7.74
33	7.19

Heating also reduced the viscosity as evidenced in the data below for a 0.49 per cent mucilage.

[37] J. Buchanan, E. E. Percival, and E. G. V. Percival, *J. Chem. Soc.*, 51-54 (1943).
[38] Margaret R. Butler, *Biol. Bull.*, **73**, 143-46 (1937).
[39] W. Clayton, "Colloid Aspects of Food Chemistry and Technology," J. & A. Churchill, London, 1932.
[40] Paul Haas and Barbara Russell-Wells, *Biochem. J.*, **23**, 425-29 (1929).
[41] A. Gutbier and I. Huber, *Kolloid-Z.*, **30**, 20 (1922).

Minutes boiled	Viscosity
5	6.89
15	6.43
25	6.19
45	5.80
75	5.47
135	5.01
165	5.01

The marked increase in viscosity is demonstrated by the following data.

Per Cent Concentration	Viscosity
0.18	4.45
0.36	7.39
0.45	9.02
0.59	11.71
0.67	14.15
0.76	18.18
0.89	31.17
1.07	36.96

Addition of electrolytes reduced the viscosity of the solution until a constant value was reached, at about 0.12 *N* for hydrochloric acid, sodium hydroxide and sodium chloride.

de Jong and Gwan[42] found that the viscosity of Irish moss solutions is extremely sensitive to electrolytes, being greatly decreased by low electrolyte concentrations, up to milliequivalent. Valence of the cation is an important factor here. The authors postulate that the decrease in viscosity by the electrolytes is of the electroviscous type.

Pfister[43] described a commercial method for the purification of Irish moss. For removing soluble impurities and obtaining a purified product of high viscosity, an aqueous Irish moss solution is treated. The gum is precipitated free of soluble impurities. Mechanical separation is made from the impurity-containing liquid. Drying of the precipitate is carried out with no more than mild heat. Purification results from passing successive small increments of the gum solution into a large body of alcohol while effecting thorough physical division of the dissolved and precipitating gum relative to the alcohol. An arrangement of application is described. Blihovde[44] also describes an arrangement of application and a process of refining and purifying Irish moss gum which involves treating a solution containing about 10 per cent of the gum with alcohol and subjecting the precipitating gum, while under the precipitating action of the alcohol, to comminution, to produce a precipitate in comminuted form for

[42] H. G. B. de Jong and O. S. Gwan, *Kolloidchem. Beihefte*, 29, 436 (1929).
[43] A. Pfister, U. S. Patent 2,231,283 (Feb. 11, 1941).
[44] N. Blihovde, U. S. Patent 2,231,284 (assignor to Jacques Wolf & Co.) (1941).

facilitating mechanical separation of the liquid, and thereafter separating the liquid, to obtain a residue which may be readily dried to produce a purified product of high viscosity.

Lawall and Harrisson[45] experimented with the bleaching of Irish moss with sulfur dioxide.

Leon[46] suggested that the thickening properties of Irish moss extracts could be stabilized and increased by the addition of alkali or alkaline earth salt.

Algin and Alginates

In 1883 E. C. C. Stanford, an English chemist, was attracted to the kelp industry, then a source of iodine. Stanford became interested in seaweed as a raw material for chemical products and pioneered in this field. His attempts led him to produce these as by-products of iodine extraction. In this he was unsuccessful, but his discovery of alginic acid is the basis of present day manufacture. During his work seeking to improve his yields of chemicals, Stanford obtained by alkaline extraction a substance with unusual gelling properties. When the material was precipitated, filtered, and purified, Stanford found it to be an acid and named it after the algae—alginic acid.

Alginic acid is a dry substance and not a liquid. Under microscopic examination it is seen to be fibrous in a manner similar to that of cellulose or wood pulp.

In Stanford's "wet" process, as originally developed, the kelp or seaweed was washed with cold water to dissolve the soluble salts, particularly those of potassium and the iodides. The mass was digested for 24 hours with 10 per cent of its weight of soda ash (sodium carbonate) while either cold or warm. A gelatinous mass resulted from this treatment. The slurry was filtered to eliminate foreign material and cellulosic matter. The alkaline filtrate was neutralized with hydrochloric or sulfuric acid. Alginic acid precipitated in light gray gelatinous flocs. These were washed and pressed in a wooden screw press to form a crumby, semi-compact cake. Treatment of the cake with sodium carbonate converted it into sodium alginate. This was stable and when dried appeared to be composed of thin, almost colorless sheets resembling flake gelatin, but with greater flexibility as compared to gelatin.

The algin industry has expanded greatly since Stanford's development. It is estimated that the United States production is well over 2,000,000 pounds per year with a value of over one and one-half million dollars.

[45] C. H. Lawall and J. W. E. Harrisson, *J. Am. Pharm. Assoc.*, 21, 1146-53 (1932).
[46] J. H. Leon, French Patent 680,188 (Aug. 12, 1929); German Patent 546,543 (Dec. 15, 1929).

Algin products may be in the form of crude pastes as used in boiler water treatment selling at 5 to 7 cents per pound or in purified algin dry flakes at 80 cents to a dollar or more per pound.

On the European and American coasts of the Atlantic Ocean, the horsetail kelp, *Laminaria digitata* and the broad-leaf or sugar kelp *Laminaria saccharina* are harvested as raw materials. Gathering is by power boats equipped with grapple hooks so as to operate at depths of 12 to 15 ft. Lesser quantities are collected from dories by hand dragging and raking as off-season work by fishermen. The best season for collection is from June to the early part of December. The Algin Corporation of America uses these algae at its plant at Rockland, Maine, to produce a purified algin and derivatives.

On the Pacific Coast of the United States, the giant kelps, growing to over 100 ft. in length and forming beds many square miles in area in the sea, are harvested as the algin raw material. Commercially the *Macrocystis pyrifera* has been collected in amounts of several hundred thousand tons a year south of Point Conception, California. The gathering mechanism is a motor-driven barge on which a modified underwater mowing machine is mounted. The machine has a horizontal blade, 10 to 20 ft. wide, set about 4 to 5 ft. below the water surface. The kelp after it is cut is hoisted aboard by an inclined chain elevator. The cutter is mounted on the bow of the boat so that the cutting knife is ahead. The boat at its beam is wider than the cutting knife. The gatherer or elevator is set directly in back of the knife. It is chain-driven at speeds which are high enough to collect the kelp before the motion of the water carries it away. The edges of the elevator are equipped with knives for "edge" cutting so that the kelp does not jam at the sides and clog the cutter and elevator. Barge capacities of 300 tons of kelp are not unusual. Kelp "farming" is carried on by cyclic cutting of the beds to allow growth periods and natural replenishment.

The major manufacturing processes are those of Kelco Co. whose plant at San Diego, California, uses *Macrocystis pyrifera,* which process is covered by the Green, U. S. patent 2,036,934; and that of the Algin Corporation of America whose plant is at Rockland, Maine, and whose raw material is *Laminaria,* and whose process is indicated in the Le Gloahec and Herter, U. S. patent 2,128,551. In the Algin Corporation process, calcium chloride is employed as a leaching agent, while calcium alginate is formed in the Kelco Co. procedure at a different stage. In the Algin Corporation process, clarification is continuous or semi-continuous through an aeration and centrifuging series of steps in contrast to the Kelco utilization of filter-aids and plate and frame filters. The Algin

Corporation process makes use of an inorganic jelly which sorbs pigments and decolorizes the alginate. Each process will be discussed in detail.

The flowsheet of the Kelco Co. operations is shown in Figs. 36 and 37.

The Kelco process avoids heating of solutions and most of the operations are conducted at 50°F. The fresh kelp is leached with a weak hydro-

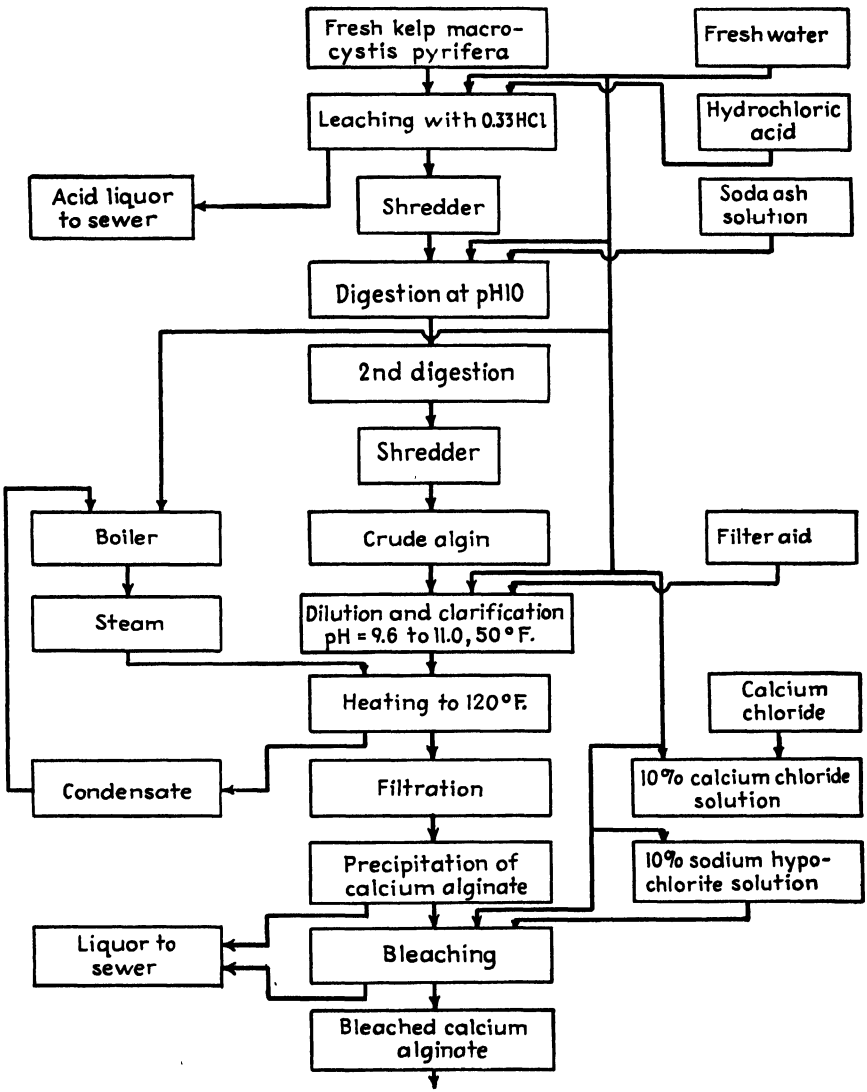


FIGURE 36. Flowsheet of alginate preparation—Part 1.

chloric acid solution for several hours until the salt content of the kelp is reduced. The kelp is separated from the liquor (which drains off to waste) and chopped up and then shredded. The comminuted product is digested for about 30 minutes with about 40 to 50 lb. of soda ash per ton

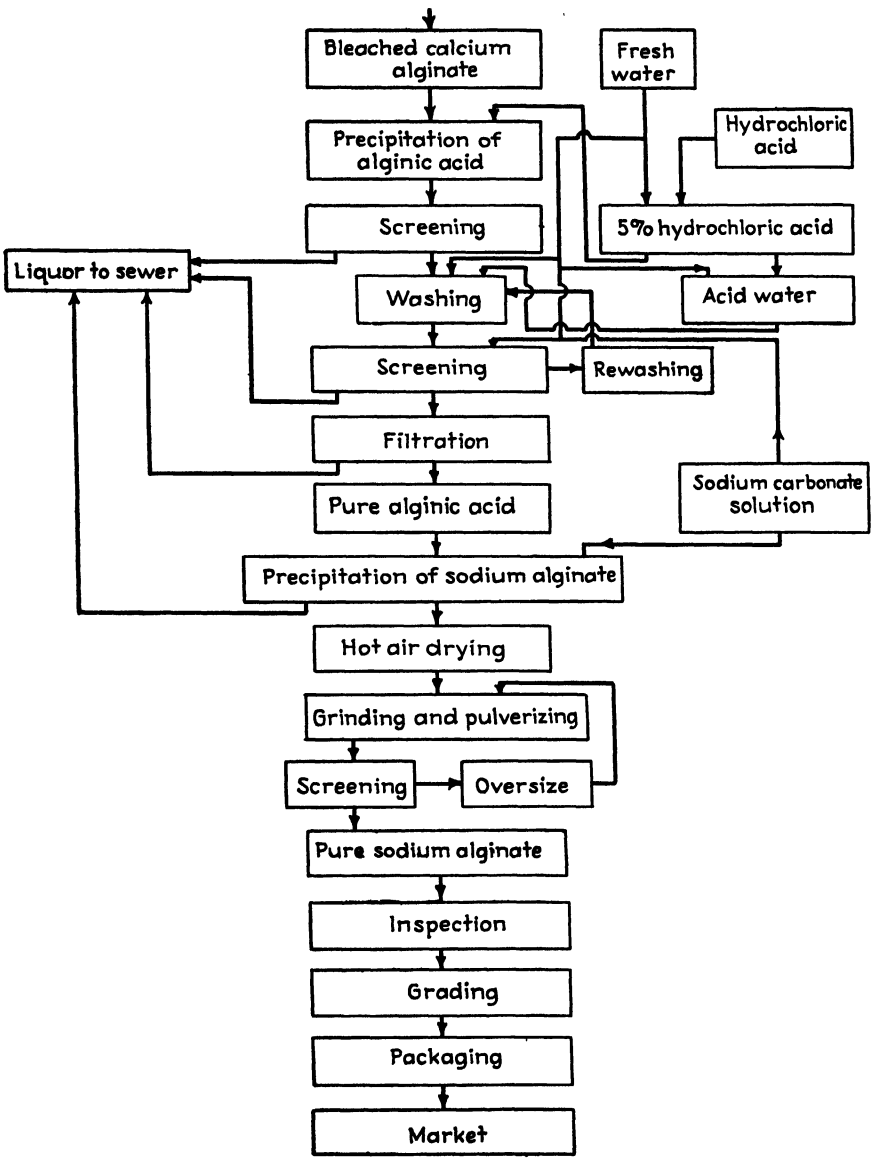


FIGURE 37. Flowsheet of alginate preparation—Part 2.

to give a pH of about 10. The somewhat gelatinous mass is given a similar second digestion while cold. The pulp at this stage passes through a hammer mill and is disintegrated. Approximately six volumes of water are added and chemical control maintains the pulp at a pH of 10.6 to 11.0.

For some industrial uses (such as treatment of boiler-feed water) the material at this stage is satisfactory and useful. The fibrous material may be dried and sold as a crude sodium alginate.

For further purification, separations of the cellulose and impurities, the liquor and suspended solids are pumped to a clarification tank. Filter aids of the diatomaceous earth type are added. The clarifying agents are mechanically stirred in and allowed to settle. The supernatant liquor is pumped through a plate and frame type filter press. If clarification is not easily done, the liquor may be preheated before filtration to aid the process.

As a purification step the soluble sodium alginate is precipitated as the calcium salt by the addition of filtered sodium alginate liquor to a solution of approximately 10 per cent calcium chloride. Approximately 12 to 15 lb. of calcium chloride is added per ton of alginate liquor. High speed agitators serve to bring the reagents into close contact. The precipitated calcium alginate is lighter than the solution and floats to the top. The lower layers of water containing soluble salts and soluble organic matter are drained off to waste.

The "curd" of calcium alginate is washed with fresh water and bleached with a 1 per cent sodium hypochlorite solution. Excessive bleaching is avoided. The stock is separated from the bleach liquors and allowed to drain.

The calcium alginate is converted to fibrous alginic acid by treatment with 5 per cent hydrochloric acid solutions. Usually 42 parts of solution are required for each unit of alginate. Excess acid and the calcium chloride formed by the reaction are removed by passing the slurry to a screen to drain. The fibrous precipitate is rewashed with acidulated water, agitated, rescreened, and allowed to drain. Washing with hydrochloric acid solutions is continued until the calcium content has been sufficiently reduced.

The alginic acid is somewhat unstable and sensitive to temperature changes so that storage is under refrigeration conditions. Conversion by treatment with sodium carbonate to sodium alginate gives a stable product which may be dried and shipped. Reaction with the carbonates, oxides or hydroxides of other metals gives corresponding alginates which may be dried, screened, ground and packaged to be employed as such or components of mixtures.

The Algin Corporation process is outlined in Figs. 38, 39, and 40.[47] It utilizes the selective solvent effect of dilute solutions of alkaline-earth salts on the lamarin and mannitol constituents of the seaweeds. Calcium chloride is preferred in that it is cheap and available in large quantities.

The raw material is *Laminaria* either fresh, when available, or in the dried, baled form from storage. Three volumes of 0.8 to 1.0 per cent calcium chloride in fresh water is added to 1 volume of dry seaweed or to its

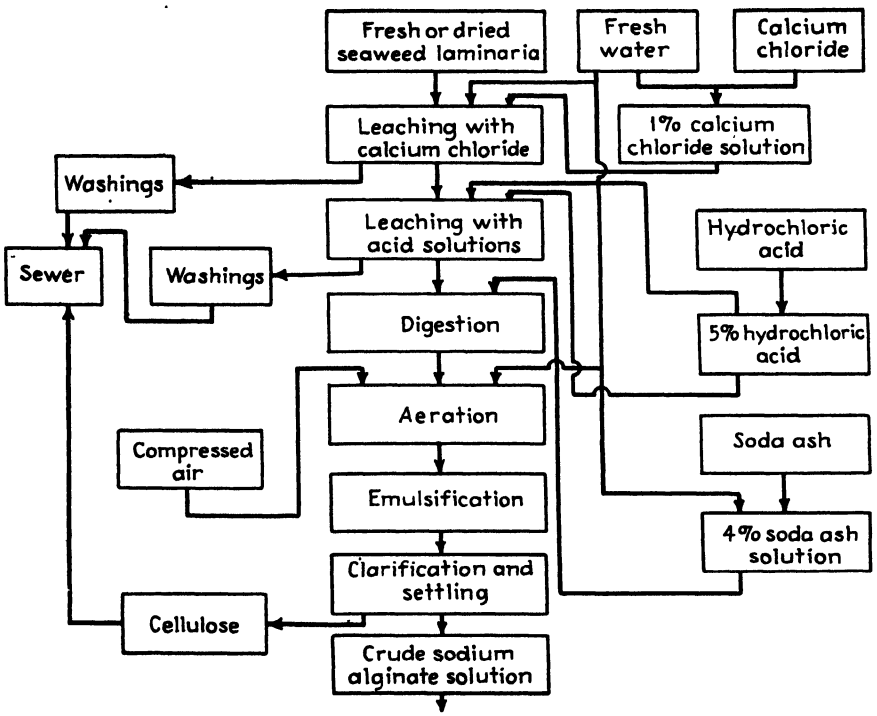


FIGURE 38. Algin Corporation process—Part 1. Preparation of crude alginate solution.

wet equivalent. Cold leaching is preferred. After this operation the seaweed is washed with fresh or softened water to remove soluble materials as well as any calcium chloride. Washing ceases when the waste waters contain about 0.5 per cent soluble materials. Any residual alkalies and alkaline-earth salts may be eliminated by treatment with a dilute (5 per cent) hydrochloric acid solution, followed by further washing with fresh or softened water.

The seaweed is treated and digested with a 4 per cent soda ash solu-

[47] V. C. E. Le Gloahec and J. R. Herter, U. S. Patent 2,128,551 (Aug. 30, 1938).

tion in the proportion of 2 volumes of soda ash solution to 1 volume of seaweed. Digestion follows paper mill practice to a degree as hollanders and pulp beaters are often used. Beating is continued until a homogeneous paste is formed and the cellulose of the seaweeds mechanically broken down. This operation is accelerated by increased temperature. A typical batch might take 3 hr. at room temperature and only 2 hr. at 105 to 110°F.

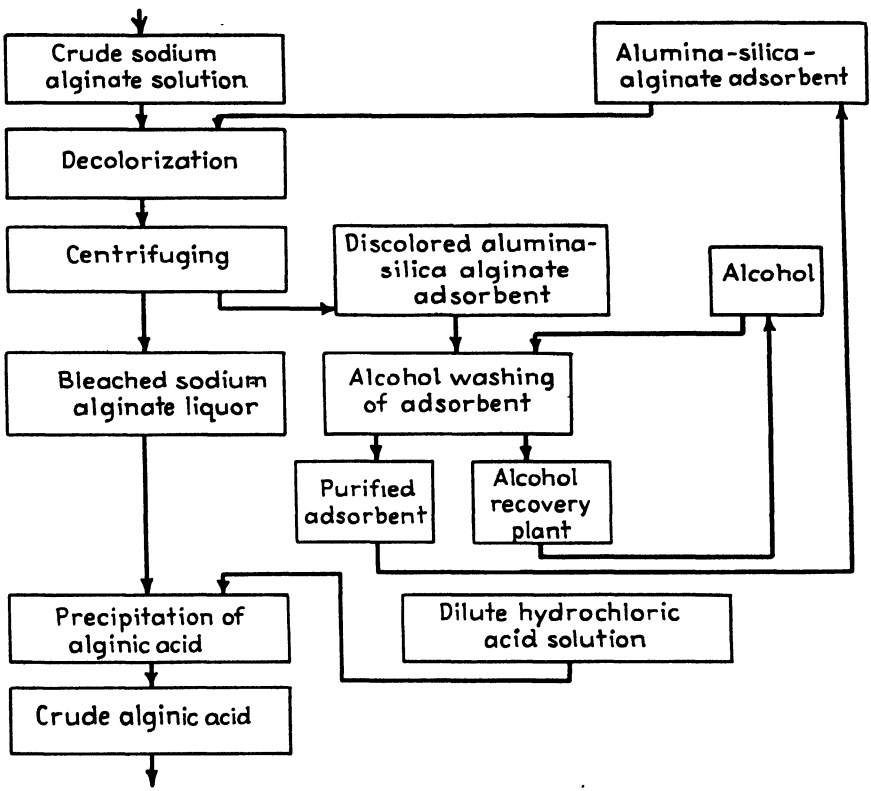


FIGURE 39. Algin Corporation process—Part 2. Preparation of crude alginic acid.

The paste is diluted so that about a little more than twice the volume of water is added. Beating converts the mixture to a more or less uniform suspension. Compressed air is pumped in through fine openings or in perforated pipes or porous diffuser plates to provide vigorous stirring. There is some evidence that oxidation by the air makes a higher viscosity product. Various mechanical means have been suggested so that an emulsion of the diluted seaweed paste results. The emulsion is transported or pumped to a clarification and settling tank where after a 6 to

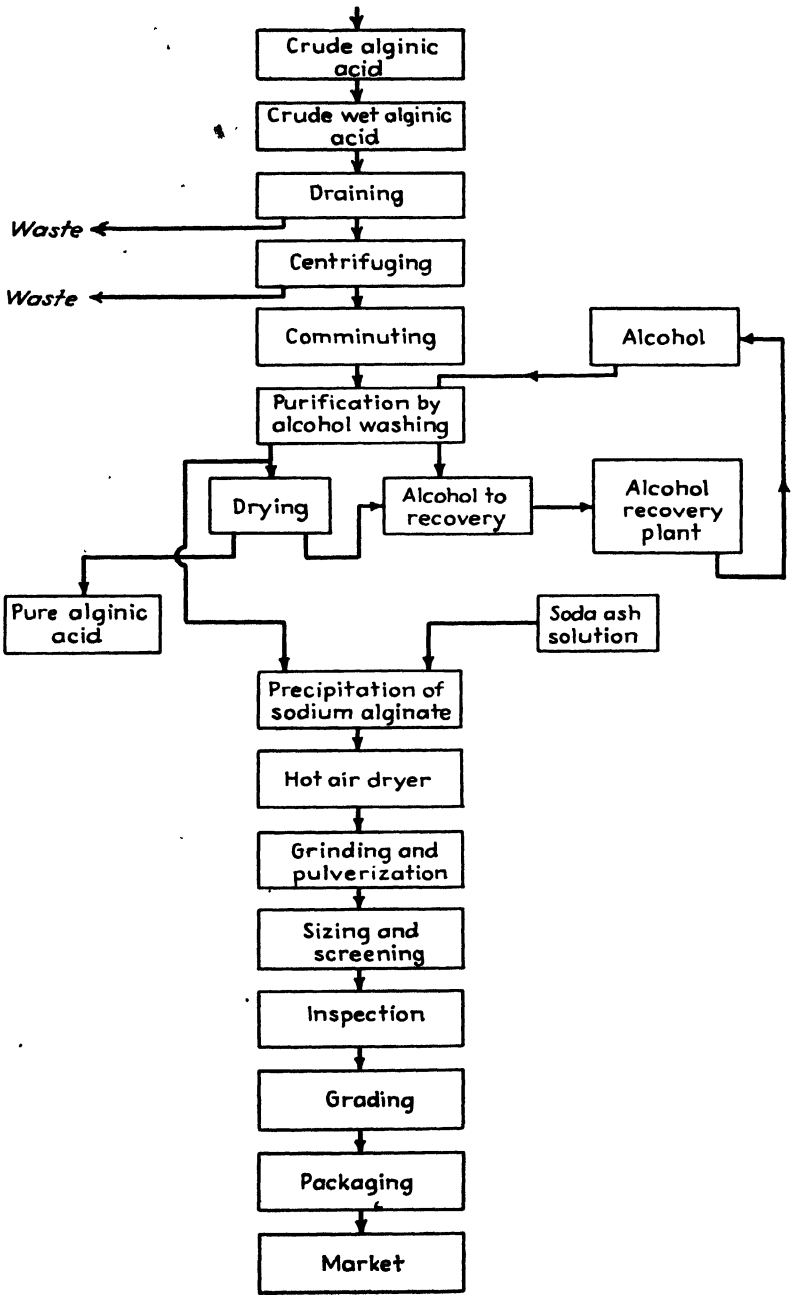


FIGURE 40. Algin Corporation process—Part 3. Preparation of refined sodium alginate.

12 hr. period the cellulose particles floc together, rise to the top of the liquor and form a compact floating cake. This may be skimmed or drained off or else the underlying liquid layer containing the crude sodium alginate liquor may be pumped to storage or on to further steps in the process.

The crude liquor carries the color resulting from the soda ash extraction, which extraction also causes some of the seaweed pigments to pass into solution or suspensions. These colors must be removed so that a white product may be made. Various adsorbents[48] may be employed but a floc collecting jelly somewhat analogous to the "Schmutzdecke" of the sand filter of a potable water plant is preferred. This adsorbent jelly is a mixture of colloidal hydrated alumina or aluminum hydroxide, gelatinous or hydrated silica and aluminum alginate. Approximately one-quarter as much jelly is used equivalent to the dry weight of the sodium alginate present. When intimate mixture is obtained the pigments are selectively adsorbed by the jelly and removed by centrifuging, leaving the sodium alginate behind. The jelly may be purified by extracting the seaweed pigments such as chlorophyll or the like with alcohol, returning the jelly for cyclic reuse, the alcohol going to a still for recovery.

The sodium alginate liquor is now carefully clarified either by fine filtration or centrifuging. The sodium alginate is converted to alginic acid by the addition of hydrochloric acid in controlled amounts. The alginic acid overflows to a wash tank. After collection and drainage, the alginic acid is dewatered in a high-speed centrifuge, broken up into small lumps or pieces and washed with alcohol on porous plate stationary filters. The washed and purified alginic acid may be dried at 150 to 170°F. and prepared for the market or it may be converted into pure sodium alginate following the same steps as at the end of the Kelco process.

The Chemical Constitution of Alginic Acid. Nelson and Cretcher[49] studied the alginic acid from *Macrocystis pyrifera* and reviewed the earlier work. Stanford[50] thought algin contained nitrogen, but Krefting,[51] and Hoagland and Lieb[52] have shown that when alginic acid is pure it is nitrogen free. Kylin[53] isolated acidic materials from the seaweed and reported that acid hydrolysis of alginic acid apparently gave only pentoses. Hoagland and Lieb[54] prepared pure alginic acid from *Macrocystis pyrifera* and found the neutralization equivalent to be 325, and reported

[48] C. L. Mantell, "Adsorption," McGraw-Hill Book Company, Inc., New York, 1945.
[49] W. L. Nelson and L. H. Cretcher, *J. Am. Chem. Soc.*, **51**, 1914-22 (1929).
[50] *Chem. News*, **47**, 254, 267 (1883).
[51] English Patents, **11**, 583 (1896); **12**, 416 (1898).
[52] *J. Biol. Chem.*, **23**, 287 (1915).
[53] *Z. physiol. Chem.*, **83**, 171 (1913); **94**, 337 (1915).
[54] *Op. cit.*

a compound having a formula $C_{21}H_{27}O_{20}$ containing two replaceable hydrogen atoms. Atsuki and Tomoda[55] suggested that glucuronic acid was the acid nucleus in algin. Their reasoning for the existence of a uronic acid was based on the observation that their algin lost 20 per cent of its weight as carbon dioxide when boiled with hydrochloric acid. Schmidt and Vocke[56] claimed to have isolated *d*-glucuronic acid from hydrolyzed alginic acid from *Fucus serratus*. Nelson and Cretcher[57] check this work and conclude that the acid present is of the type containing six carbons and an aldehyde group. Their carefully prepared algins from *Laminaria* and *Macrocystis* gave neutralization equivalents of 176 to 184, while carbon and hydrogen determinations indicated a formula of $(C_6H_8O_6)_n$. Boiling with hydrochloric acid liberated 24 to 25 per cent of carbon dioxide. The acids do not reduce Fehling's solution. They conclude that algin is a polyuronic acid in which all carboxyl groups are free and all aldehyde groups conjugated.

Pure alginic acid is very slightly soluble in water. It reacts with carbonates to produce carbon dioxide and may be titrated with an alkali to an end point as given by an indicator such as phenolphthalein. It does not give the reducing sugar reaction with Fehling's solution, but if dried at 100° or boiled with water or dilute acid it may be converted into reducing substances. Its optical rotation and acid value vary as a function of the temperature at which it was dried and the time taken for this operation. Sodium alginate is stated to have an optical rotation of $[\alpha]_D^{20} = -133°$.

Alginic acid may be considered an anhydride of an aldehyde sugar acid in which all the carboxyl groups are free and all the aldehyde groups conjugated.

Lunde, Heen and Oy[58] prepared alginic acid and found the average carbon dioxide content of several preparations was 24.3 per cent. Kringstad and Lunde[59] prepared threads of alginic acid. They state that the X-ray diagrams of the threads indicate a definite structure which is analogous to that of cellulose. Heen[60] calculated the molecular weight by the viscosimetric method and reported a figure of 14,100 for alginic acid and 15,400 for sodium alginate.

Barry and Dillon[61] give a formula of $C_6H_{10}O_7$ for alginic acid, the sodium salt of which shows an optical rotation value of $[\alpha]_D^{10} = -132.6°$. They report that the analysis of the barium salt and polarimetric measure-

[55] K. Atsuki and Y. Tomoda, *J. Soc. Chem. Ind. (Japan)*, **29**, 509 (1926).
[56] E. Schmidt and F. Vocke, *Ber.*, **59**, 1585 (1926).
[57] *Op. cit.*
[58] G. Lunde, E. Heen, and E. Oy, *Kolloid-Z.*, **83**, 196-202 (1938).
[59] H. Kringstad and G. Lunde, *Ibid.*, 202-203.
[60] E. Heen, *Ibid.*, 204-210.
[61] V. C. Barry and T. Dillon, *Sci. Proc. Roy. Dublin Soc.*, **21**, 285-7 (1936).

ments of the sodium salt support the assumption that the polymerizing unit in alginic acid is the complete uronic acid and not the anhydride.

Miwa[62] concluded from his studies of alginic acid from four different varieties of seaweed that they all produced mannuronic acid.

Because of its high alginic acid content and the ease of preparation from *Undaria pinnatfida*, Miwa[63] considers this the best of the brown algae as a source of this acid. The purified product is ash and nitrogen free and shows the naphtho-resorcinol reaction characteristic of uronic acid. Direct titration required exactly three-quarters as much alkali as addition of excess and back titration, suggesting a lactone structure. This and analysis for carbon and hydrogen suggest the formula $C_{24}H_{30}O_{23}$. The equivalent weight (177-9) and $[\alpha]_D - 133.1°$ check the values found by Nelson and Cretcher.[64] The alginic acid obtained by Miwa is non-reducing but becomes reducing on hydrolysis. Hydrolysis yields a uronic acid, isolated as the cinchonine (melting point 175°C. with decomposition, $[\alpha]_D^{12}$ 130.6°) and brucine salt (melting point 175°C. with decomposition, $[\alpha]_D - 25.6°$). Oxidation of the uronic acid with bromine and nitric acid gave mannosaccharic acid. Hydrolysis by the methods of Nelson and Cretcher and of Schmidt and Vocke[65] gave the same cinchonine salt, but by one of the methods of Bird and Haas[66] hydrolysis gave the same cinchonine salt and in addition an easily recrystallized salt melting at 212°C. ($[\alpha]_D^{13}$ 94.7°). The nitrogen and cinchonine contents and the reducing power suggest that this may contain 2 mols. of mannuronic acid. Hydrolysis of alginic acid obtained from eight different plant sources yielded the same cinchonine and brucine salts as from *Undaria pinnatfida*.

Heen[67] concluded that alginic acid has the formula $(C_6H_8O_6)_n$ with a molecular weight of 15,000, and that it consists of condensed hexuronic acid residues having a structure very like that of cellulose but with the radical COOH replacing CH_2OH. It can be considered as a link between the homopolar celluloses and the heteropolar proteins.

Gomez[68] states that alginic acid from *Fucus vesiculosus, Laminaria flexicaulis*, and *Ascophyllum nodosum*, by extraction with sodium carbonate and precipitation with hydrochloric acid, is thermostable, carbonizes at 250 to 300°C. after softening at 180°, has an acid number of 194, and contains ash varying in different preparations from 0.47 to 2.5 per cent, depending on the source and method of purification. The ash

[62] T. Miwa, *J. Chem. Soc. Japan*, **51**, 738-45 (1930).
[63] T. Miwa, *Sci. Repts. Tokyo Bunrika Daigaku* B1, No. **2**, 23-37 (1932).
[64] W. L. Nelson and L. H. Cretcher, *J. Am. Chem. Soc.*, **52**, 2130-32 (1930).
[65] E. Schmidt and F. Vocke, *Ber.* **59B**, 1585-88 (1926).
[66] G. M. Bird and P. Haas, *Biochem. J.*, **25**, 403-11 (1931).
[67] E. Heen, *Tids. Kjemi Bergvesen*, 17, 127-29 (1937).
[68] M. L. Gomez, *Inst. espan. oceanograf. Notas y resumenes* Ser. II, No. **74**, 98 pp. (1933).

consists of aluminum, calcium, and magnesium. This appears not to be bound in salt formation and is incompletely removed by dialysis. Gomez states that alginic acid has the same strength as monochloracetic acid.

Pauli and Sternbach[69] prepared highly purified sols of alginic acid by electrodialysis and electrodecantation and both acidoid and neutral alginate sols were characterized by electrochemical and viscosity measurements. The effect of cautious as compared with vigorous preparation of the sols manifests itself in the formation of a hydrated form with ($C_6H_{10}O_7$) chain members with the acid equivalent $S^* = 194$. Conductivity titration is the best method of determining S^*, which is the ratio $(c - \text{ash})/c_H$, c being concentration in grams per liter and c_H the normality of acid at the second break in the titration curve. The alginic acid sols behave like colloidal electrolytes of multivalent character in that the H^+ activity and degree of dissociation measured potentiometrically exceed those measured conductometrically. After decomposition of the sols by boiling, they exhibit the typical behavior of dilute uni-univalent electrolytes. The degree of dissociation of the acidoid sols attains a constant value on dilution corresponding to a sharp decrease in the classical dissociation constant with decreasing concentration, as is the case with sols of other vegetable gums.

Takahasi[70] and Takahasi and Okawara[71] studied the formation of films and fibers of alginic acid. All of the films require treatment with heavy metal salts to improve their properties. Onokhin and Lipinskii[72] studied the use of ammonium alginate as a starting material in the production of plastics. These needed thermal treatment to increase the resistance to water. Pribytkova[73] prepared alginic acid fibers and films and found that they all swelled in water, while the films of the copper, calcium, zinc, aluminum, iron, and lead alginates were very brittle.

Tsimehc[74] states that the calcium and aluminum alginates disappear in soap and soda solutions in contrast to the chromium and beryllium alginates. Fabrics made of beryllium alginate threads resist burning.

Algin or sodium alginate is commercially important because of its properties as an emulsifying, suspending, jellying, thickening, and bodying agent. It is believed that one of the largest uses of algin in the United States is as a stabilizer for ice-cream. Its presence induces smoothness of

[69] W. Pauli and L. Sternbach, *Kolloid-Z.*, **84**, 291-303 (1938).
[70] T. Takahasi, *Rayon World* (Japan), 7, No. 11, 11-18 (1939).
[71] T. Takahasi and N. Okawara, Japanese Patent 133,534, Nov. 29, 1939, assigned to Tokyo Kogyo Sikenzyotyo.
[72] I. P. Onokhin and M. A. Lipinskii, *Trudy Arkhangel. Vodoroslevogo Nauch.—Issledovatel. Inst., Vodorosli Belogo Morya* (1938), 196-220; *Chem. Zentr.* (1939), II, 524.
[73] N. A. Pribytkova, *Trudy Arkhangel. Vodoroslevogo Nauch.—Issledovatel. Inst., Vodorosli Belogo Morya* (1938), 175-87; *Chem Zentr.* (1939), II, 524.
[74] A. Tsimehc, *Silk J. and Rayon World*, 17, No. 198, 13-14 (1940).

body and texture, serving as a restraining colloid, preventing the growth of ice crystals during storage. Algin finds wide application in food products of a foam, jelly or emulsion nature such as cakes, icings, chocolate milk, and whipping cream. Matthews[75] gave formulae for the use of sodium alginate in hand emollients. Martell and Schaller[76] patented alginate milk products such as ice-cream and milk mixtures.

Hauser and Dewey[77] discussed the application of ammonium alginates in the creaming of rubber latex, particularly synthetic rubber materials. Preble[78] employed triethanolamine alginate as a coating for cheese, meat, and other food products, alone or in combination with other compounds. Bergy[79] gave formulae for the use of sodium alginate in toothpastes, lotions, pastes and polishes, while Cate[80] studied the application of sodium alginate in cold-water or emulsion paints. Sodium alginate paints show a slight yellowing on ageing. Haddan[81] proposed the addition of an edible soluble alginate to bread and bakery products, while Takahasi[82] experimented in the application of alginic acid in textile processes. Musick[83] gives formulae for hand lotions containing sodium alginate, which material supplies the "slip."

Ammonium and sodium alginates have been widely suggested for casein emulsion paints. Sodium alginate, particularly in its cheaper and cruder form, is employed as an addition to boiler feed water to prevent incrustation. Calcium alginate precipitates are formed with the alkaline earth compounds in the water to give globular flocculent masses. These, with other compounds which settle out, give a soft pasty sludge which can readily be "blown down."

Algin and sodium alginate in many ways compete with the natural gums such as arabic and tragacanth in the preparation of greaseless lubricating jellies, hand lotions, sizing materials, pharmaceuticals, and the many products which require thickening agents where viscosity increases are produced with small increases of solids content. Being the product of chemical manufacture, the alginates are more consistently uniform than are the natural gums.

Considerable research on alginates as textile fibers has been carried forward. Table 17 shows the properties of the fibers. They do not compete with cotton or other natural fibers or rayon or nylon and the

[75] D. R. Matthews, *Pharm. J.*, 148, 79 (1942).
[76] Jean K. Martell and Joseph W. Schaller (assignors to Fitger California Co.). U. S. Patent 2,238,906 (April 22, 1941).
[77] E. A. Hauser and Bradley Dewey, Jr., *Ind. Eng. Chem.*, 33, 127-30 (1941).
[78] Bennett Preble (assignor to Kelco Co.), U. S. Patent 2,158,485 (May 16, 1939).
[79] Gordon A. Bergy, *Am. Professional Pharmacist*, 5, 494-95 (1939).
[80] P. H. Cate, *Am. Paint J.*, 22, 58, 60, 62 (April 18, 1938).
[81] Reginald Haddan, British Patent 525,766 (Sept. 4, 1940).
[82] Takeo Takahasi, *Rayon World* (Japan), 6 (No. 2), 17-23 (1938).
[83] Albert H. Musick. *J. Am. Pharm. Assoc., Pract. Pharm. Ed.*, 3, 264-67 (1942).

Table 17. Properties of Alginate Fibers

	Alginic Acid	Calcium Alginate	Aluminum Alginate	Chromium Alginate	Beryllium Alginate
Metal content	0.1% ash	10.38% Ca	3.30% Al 5.50% Ca	1.53% Cr 8.29% Ca	2.98% Be 4.91% Ca
Specific gravity	1.627 (dry) 1.558 (conditioned)	1.779	1.773	1.780	1.735
Tensile strength (grams per denier) r.h. 0	2.00	2.18		2.02	2.80
r.h. 65%	0.50	1.14		0.99	1.56
r.h. 100%	Too weak to determine	0.29		0.68	1.08
Extension at break (%) r.h. 0	9.7	10.1		5.6	3.9
r.h. 65%	4.3	14.3		4.2	5.2
r.h. 100%	Too weak to determine	25.7		4.5	3.2
Water adsorption r.h. 63.8%		20.4	28.5	29.1	24.9
r.h. 100%		51.9	54.5	61.8	53.0
Effect of heat	Will not burn	Will not burn	Will not burn	Will not burn	Will not burn
Effect of alkali	Dissolves	Dissolves	More resistant, Dissolves in 1 hr.	Highly resistant	Highly resistant
Effect of age	Deteriorates greatly after about 130 days	Stability increased with increasing pH		Improved during storage at 65% r.h. and 22.22°C.	Improved during storage at 65% r.h. and 22.22°C.
Remarks		Easy to weave, useful as stock material	Not satisfactory	Necessary degree of alkali resistance for general use, but too highly colored	Necessary degree of alkali resistance, not colored

Textile World, 95, No. 12 (1945).

synthetic group, as they readily dissolve when washed with soap or alkalies. They are of some interest in textile fabrication in designs which utilize the fibers in weaving and remove them by solution in finishing to obtain effects otherwise not possible. The preparation of fibers and yarns and the weaving thereof, with removal at a later stage, is a relatively expensive procedure which can be justified only in the case of special and costly fabrics.

Chapter 7

The Hemicelluloses: Locust Bean Gum, Seed Extracts, and Iceland Moss

The hemicelluloses are chemically related to the cellulose compounds, the simple sugars, and the starches, and occupy an intermediate position. They swell up enormously when heated with water and thus serve as thickeners in the same way as the gums do. They pass into the stage of colloidal sols which may show very high viscosity. Normally, through lack of stability, the sols must be made up fresh, inasmuch as they revert to gels which are non-rigid after a few days' standing.

The hemicelluloses embrace a group of substances which are closely related chemically and which are contained in the seeds and fruits of various plants. The cellular tissues of these plants consist largely of products intimately associated with cellulose and chemically allied thereto. The hemicellulose materials which find commercial application are locust bean gum, locust kernel gum, guar and extracts of seeds such as those of the quince, psyllium, flax, in relatively large quantities and miscellaneous other seeds in smaller amounts, as well as lichens such as Iceland moss.

The hemicelluloses vary widely in composition. Solutions yield clear transparent continuous films on evaporation. Many of these show considerable tensile strength and are tougher than films of medium viscosity nitrocellulose. Stocks and White[1] give the approximate formula $C_6H_{10}O_5$. They contain little mineral matter and are usually non-acidic in their chemical reaction. Water extracts of the hemicellulose are sols showing a very high viscosity, increasing greatly with increases in concentration, while the application of heat shows only a slight effect on decreasing the viscosity. The mineral acids markedly affect the viscosity, dilute acids very considerably lower it. In general, the alkalies particularly increase the viscosity of strong sols which become almost glutinous or stringy. The effect of salts and electrolytes is slight except in concentrated solutions where precipitation may occur in many cases. The salts of heavy metals, particularly those of iron and copper, as well as oxidizing agents such as hydrogen peroxide, sodium peroxide, and the

[1] H. B. Stocks and H. G. White, *J. Soc. Chem. Ind.*, 1903-4

persulfates, reduce the viscosity of hemicellulose sols. Thermal treatment under pressure as well as in the presence of organic acids renders the colloidal dispersions fairly fluid, but on standing some reversion takes place.

Adsorption complexes are formed between the hemicellulose sols and bases such as those of the alkaline earth metals. These show greater solidity with increase in concentration, while in diluted sols precipitation takes place. Basic lead acetate forms a heavy solid white opaque gel, as do potassium permanganate and Fehling's solution. Boric acid, borax, and boron compounds cause the sols to become viscous gels, the viscosity increasing to such a point that flow ceases. The surface tension may become so high that water will not penetrate. High-speed and vigorous stirring breaks the gel up into small particles which gradually show water absorption and become homogeneous again.

Mixtures of hemicelluloses are readily made with pastes of starches, dextrins, the seaweed colloids, and with some care in the concentration these may be made homogeneous. With gum arabic, the gums, gelatin, and strong solutions of dextrin, the hemicelluloses tend to form granular or frothy heterogeneous mixtures which sooner or later separate.

A number of hemicelluloses react with tannic acid to form interesting complexes. These in the presence of excess tannic acid show the appearance of an opaque turbid sol, with considerable reduction in viscosity right after the two are mixed. On standing for some time the viscosity rapidly increases until after a few hours a soft gel is formed which conforms to the shape of the vessel containing the gel. After a further period of time the material separates into a gel of greater stiffness and a clear supernatant liquid. Upon removal from the liquid, the gel progressively dehydrates until it forms a tough leather-like material which on complete drying is a hard solid. This is an adsorption compound containing $C_{14}H_{10}O_9$ and $C_6H_{10}O_5$ molecules in the proportion of 1:2. C. V. Greenwood[2] proposed that the materials be used for tanning in that the colloidal carbohydrates had a restraining influence on the tannic acid so that concentrated tanning liquors could be employed at the beginning of tanning and thus shorten the tanning period.

When the tough leather-like material is treated with water, tannic acid first dissolves, but with additions of further amounts of water the complex itself is dispersed. The tannic acid is completely dissolved by alcohol which precipitates the carbohydrate of the hemicellulose in the form of a flocculent gel. Salts such as ferric chloride, ferrous sulfate, and zinc chloride which precipitate tannic acid do not coagulate the hemicellulose hexosan-tannin complex, while lead acetate, tartar emetic,

[2] C. V. Greenwood, British Patent 5018 (1910) and 7635 (1915).

stannous chloride, sodium tungstate, and ammoniacal copper solutions coagulate it.

The turbid complex formed between sols of hemicelluloses when first mixed with tannic acid becomes more dispersed at about 42°C. with reversion to the original condition on cooling. Apparently the change is reversible.

The hemicelluloses find commercial application of the same character as the gums but differ in specific applications. They are therefore only to a limited degree competitive but are rather supplementary and complementary to the true gums, while their properties are such that they can be adequately classed with them in any general discussion.

Locust Bean Gum and Locust Kernel Gum

The locust bean gum is the dried gummy substance from the seeds of the locust bean. The locust kernel gum is the same as the locust bean gum but contains less starch and other impurities. The degree of purification varies widely in the different lots shipped to the United States since they are made in several countries and often in numerous manufacturing plants. The term locust bean gum will accordingly be employed in this book to cover in general the different products that come under a variety of names, but all of which are locust bean or locust kernel gums. Other names used to designate these gums include carob gum, carob seed gum, St. John's bread, swine's bread, gum Hevo, gum Gatto, Jandagum, Lakoe gum, Lupogum, Luposol, Rubigum, Tragon and Tragasol.

Locust bean gum is imported from Great Britain, France, and the Mediterranean area. Before 1926, only small amounts were used in the United States. In 1939, imports reached an all-time high of over 4,000,000 pounds; average annual consumption from 1929 to 1939 was somewhat in excess of 2,000,000 pounds.

The carob or locust bean tree, *Ceratonea Siligua, L.*, is widely cultivated in southern Europe, on the various islands of the Mediterranean Sea, and in northern Africa. The tree has had a long history of usefulness to mankind. Theophrastus in the fourth century B.C., in his history of plants, mentions it as being cultivated at Rhodes, while Diocorides in the first century A.D., praises the fruit as a laxative and diuretic, in his materia medica. The pods are rich in protein and sugars and form an important forage crop readily eaten by stock and by the poor in times of scarcity. The molasses and sirups are fermented to make a wine or hard liquor and for flavoring tobacco before it is cured. American imports of locust beans and pods (1,500,000 pounds in 1939) were primarily for tobacco curing and not for making the gum. The Germans use the seeds and pods to make a coffee substitute by roasting.

The pods contain about twelve red seeds from which the locust bean gum is extracted. The pods are gathered and spread out in the sun to dry, after which the seeds are removed either by hand or machine and packed for shipment.

It is said that 1,000 pounds of beans yield 100 pounds of seed, from which only 35 pounds of gum is obtained. This explains why the gum is not manufactured from imported beans. The transportation cost would be prohibitive. The removal of the gum from the seed is the subject of many patents, especially in Great Britain, all of which involve the removal of the outside skin and ovarium by passage between rollers which turn in opposite directions. Some patents specify pre-treatment of the seeds with diluted caustic soda followed by washing prior to the treatment between rollers.

One process[3] that has been successful and widely used removes the two outer coatings in the above manner and then introduces the de-hulled seeds or endosperms into a rotary oven which is heated to 150°C. and the temperature carefully regulated. When the operation is completed the seeds have attained a golden brown color. These partially de-hulled, roasted seeds are then introduced into twenty times their weight of boiling water; after two hours at the boiling temperature the heating is discontinued and the contents are allowed to cool slowly for four hours. The cooked liquor which contains the dispersed gum and traces of crude fiber is filtered through bronze screens and bags to give a transparent liquor which is evaporated by indirect heat to a moisture content approaching 25 per cent. At this point the product is a pasty solid. It is spread out on trays and further dried in a hot air current dryer. When the proper dryness is attained, the material is brittle and is pulverized and packaged. Solutions of locust gum are also sold. They are generally about 4 per cent concentration and contain a preservative such as formaldehyde or phenol.

Research on the chemical structure of the locust bean gum reveals that it does not contain uronic acids and pentoses like the tree exudates, e.g. gum arabic or tragacanth, nor acid groups like those in agar-agar or Irish moss.

Effront[4] investigated the mucilaginous carbohydrate from the carob bean which he called "caronbine." He obtained by hydrolysis a sugar which he called "caronbinose" which van Ekenstein[5] claimed to be mannose. Marliere[6] reported the carbohydrate to consist of glucose, fructose

[3] C. F. Mason, *Chem. Industries*, 54, 66 (1944).
[4] Effront, *Compt. rend.*, 125, 38, 309 (1897).
[5] van Ekenstein, *Compt. rend.*, 125, 719 (1897).
[6] Marliere, *La Cellule*, 13, 7 (1897).

and galactose, and that mannose was absent. Bourquelot and Herissey[7] reported the gum as composed of 83.5 per cent mannose, and 16.5 per cent galactose. Iglesias[8] stated the gum consists exclusively of four molecules of mannose to one of galactose and demonstrated that uronic acids are absent. Gortner and Lew[9] found that the gum consists of three to four molecules of mannose to one of galactose, and also found evidence of the presence of 1, 2 linkages. Galactose linkages are probably in the A form, while mannose linkages are probably in the B form. These authors postulate that the molecule consists of a mannan chain of six to eight mannose units followed by two galactose units and so on to a total of about eighteen hexose units.

Knight and Dowsett[10] and Williams[11] give the following analysis of samples of the gums:—

	Knight and Dowsett	*Williams*
Galactan	29.18%	24.84%
Mannan	58.42	64.39
Pentosans	2.75	4.07
Proteins	5.29	2.40
Nitrogen	0.83	0.39
Cellular tissue	3.64	1.46
Mineral matter	0.82	2.81
Ceratoniase (enzyme)	present	

Gutbier[12] found the gum is negatively charged in water and studied its protective action on metal sols.

Williams[13] and Hart[14] show that the gum is precipitated by basic salts but not by normal salts except at high concentrations. Fehling's solution is not reduced by the gum but yields a blue gelatinous precipitate soluble in dilute acids. Alcohol precipitates the gum complex from its aqueous solutions as a white gelatinous mass.

When dissolved in water locust bean gum forms viscous solutions or heavy opaque pastes depending upon the concentration. On boiling, these suspensions tend to become clear but precipitate a heavy flocculent substance on cooling. Because of its tendency to form a shell of hydrated colloid, often fairly difficult to hydrate at the center and often difficult to break down the lumps, the locust bean gum is best dissolved by first adding the finely ground gum gradually to cold water with vigorous stirring.

[7] Bourquelot and Herissey, *Compt. rend.*, **129**, 228, 391 (1899).
[8] G. Iglesias, *Anales, soc. espan. fis. quim.*, **33**, 114 (1935).
[9] R. A. Gortner and B. W. Lew, *Arch. Biochem.*, **1**, 325 (1943).
[10] W. A. Knight and M. M. Dowsett, *Pharm. J.*, **136**, 35 (1936).
[11] A. L. Williams, *Analyst*, **53**, 411 (1928).
[12] A. Gutbier, *Kolloid-Z.*, **33**, 37 (1923); **34**, 336 (1924).
[13] A. L. Williams, *Analyst*, **53**, 411 (1928).
[14] R. Hart, *Ind. Eng. Chem., Anal. Ed.*, **2**, 329 (1930).

After standing several hours—if concentrated solutions are being made preferably overnight—the solution is brought to a boil. A solution containing as little as 0.5 per cent gum is noticeably viscous and a paste of 5 per cent is practically non-flowing. Hart measured the viscosity of solutions of various concentrations with an ordinary 25-cc. glass pipette. The mixture was boiled and allowed to stand overnight before readings were made. His results showing the relative viscosities as a function of concentration are given in Table 18.

Table 18. Viscosities of Locust Bean Gum Solutions

Concentration of Gum %	Viscosity at 18 to 20°C. in Seconds
0.0	14
0.25	20
0.50	62
0.75	500
1.00	very thick
5.00	solid

Acids, especially the mineral acids, lower the viscosity. Alkalies increase the viscosity, especially of strong solutions which become glutinous and at the same time darken in color. Hart[15] reports that heating them in caustic soda greatly reduces the viscosity. He found that the viscosity of a solution containing 0.75 per cent dry gum and 0.5 per cent caustic soda, heated to 95 to 98°C. and cooled to 30 to 32°C. was 62 seconds compared with 145 seconds for a similarly prepared solution without the caustic. Williams states that borax converts an 0.5 per cent solution to a solid jelly but an excess of borax liquefies the solid jelly. Hart found that the effect of borax on the gum solution if both are sufficiently concentrated is to produce a solid, irreversible, transparent gel which is dry, firm and cohesive but will no longer stick to glass or other substances. Hart also found that an excess of borax did not liquefy the gum-borax gel; that while excess borax may cause separation of clear liquid, the gel formed still retains firmness, transparency and other characteristics of the gum-borax gel.

Williams[16] reports that when a dilute tannin solution is carefully added to a solution of the gum, the gum becomes first more viscous, and then thin and milky; finally, on adding an excess of tannin, a soft gelatinous mass separates. After standing for some time the gel shrinks, taking the form of the containing vessel and finally separates into a white or buff colored clot, depending on the color of the tannin, with a clear supernatant liquid. On warming to 40 to 50°C. the whole becomes a homogeneous, highly viscous turbid mucilage if the solutions are strong, and a clear liquid if

[15] R. Hart, *loc. cit.*
[16] A. L. Williams, *Analyst*, **53**, 411 (1928).

the solutions are dilute. On cooling the precipitate again separates, and the change on heating and cooling is reversible. The precipitate is also dispersed by addition of solutions of sodium benzoate, potassium thiocyanate, alkalies and particularly by substances which contain a large number of hydroxyl groups such as glycerine and sugars. This precipitate occurs in acid solution other than acetic acid but not in alkaline solutions. Some of the tannin may be removed from the precipitate by washing with water and the whole of it by alcohol, leaving the residue in a flocculent form which can be readily dissolved in water to produce the original mucilage.

Several years ago,[17] as the result of research investigations at the Institute of Paper Chemistry in Appleton, Wisconsin, supplies of locust bean gum were required for the purpose of confirming on a commercial scale a number of observations in the laboratory. Studies with paper had revealed that locust bean gum was a valuable paper maker's adjunct in obtaining temporary wet strength in sheets such as paper toweling, and that these same gums facilitated hydration during the beating of various pulps.

A study revealed the inadequacy of supply of locust bean gum. Accordingly, an attempt was made to locate other sources of mannogalactans. The services of members of the Soil Conservation Commission of the Department of Agriculture were enlisted, and as a result, numerous seeds were investigated for their potentialities. This work revealed the existence of a plant known as the cluster bean, or guar.

Guar Gum

Guar gum is similar to locust bean gum in that it is composed essentially of the complex carbohydrate polymer of galactose and mannose. It is not, however, entirely like locust bean gum, since the ratios of these two sugars appear to be different in the two gums. The practical value of these two differences is still the subject of investigation.

Guar has been cultivated in certain sections of India for centuries as a fodder for horses and cattle. It was brought into the United States from India before World War I and it has been studied on a limited scale, primarily as a green manure.

Guar gum or guar flour is a polysaccharide which on hydrolysis yields two hexose sugars, mannose and galactose. This mannogalactan is dispersible in either cold or hot water, producing a colloidal dispersion of exceptionally high viscosity at low concentrations. A transparent film is

[17] Private communication from John S. Andrews, General Mills, Inc., Minneapolis 2, Minn.

produced when such a sol is dried, which is said to be much more flexible than a starch film.

Investigations carried out by the Institute of Paper Chemistry[18] and numerous paper manufacturers have shown that guar flour is of value as a beater additive for improving the strength of certain grades of paper. It has been said that guar possesses properties which might be useful in warp sizing, printing pastes, and in certain finishing operations. The colloidal properties it possesses enable it to serve as a stabilizer or thickener in food products such as in ice cream mixes, salad dressings, etc.

Guar is an annual plant, cultivated in a light sandy soil, and is often mixed with other vegetation. When utilized as human food, it is grown in a rich soil. It is planted during the rainy season, and harvested in the dry season of the Fall by the usual grain combine methods. There are many varieties of guar whose physical appearance and size vary. Most of the slender stalks are from 2 to 6 feet in height. The stalks bear large leaves and small pods, bean-like in shape, containing pebble-shaped seeds. The leaves fall off as the plant approaches maturity.

The outer seed coat of guar seeds is largely fibrous in nature, and is composed of at least three types of tissue in very thin layers. The endosperm contains mannogalactan with small amounts of protein, fiber, and minerals. The embryo is rich in proteins, and contains fats and sugars.

Before guar can be used, it is necessary to separate the gum-containing endosperm from the outer portions of the seed. Milling methods have been developed to achieve this purpose. Various grades of gum can be isolated, ranging from products of high purity to meet special requirements to those of lower qualities designed for the uses where high purity is not needed, but low cost is the more important.

General Mills[19] state that aqueous dispersions are practically neutral in reaction. The viscosity is somewhat affected by, but is not extremely sensitive to changes in pH or electrolyte concentration. Strong acids will cause hydrolysis and loss of viscosity. Alkalies will cause darkening particularly in the lower grade products, and some decrease in viscosity. The addition of a borax solution to a sol will bring about gelation. Alcohols, acetone, etc., precipitate mannogalactan out of aqueous sols.

If tannin[20] is added to a sol, a separation of gum tannin complex results. Redispersion may be brought about by heating, and upon cooling reprecipitation will reoccur.

As with locust bean gum, cellulose derivatives and other hydro colloids, certain techniques aid in producing a smooth dispersion.

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[18] The Institute of Paper Chemistry, Appleton, Wis.
[19] General Mills Inc., Research Dept., Minneapolis 13, Minn.
[20] The Institute of Paper Chemistry, Appleton, Wis.

Rowland[21] reports that numerous experiments have been made with guar mucilage in many mills and on many types of paper. Results indicate that guar gum in amounts of 0.5 per cent or less, based on the dry weight, imparts strength to tissue sheets in regular production.

A more resilient printing paper was obtained by the addition of 1 per cent guar mucilage to either alkaline-filled or clay and rosin-sized paper. They found that in rag content papers, both heavy and light weights, the addition of guar mucilage to the beater has demonstrated its effectiveness to be several times that of an equal amount of beater starch in building strength.

Guar can be added as a dry powder to the beater, provided the pulp receives a certain amount of beating. This has been found to be adequate in rag mills and kraft mills where the dry mucilage-containing stock was subjected to a moderate beating or jordaning action.

Flaxseed

Flaxseed gum has two properties in common with psyllium and quince gum, its water dispersibility and thickening properties. Its gum is of commercial importance in the cosmetic and pharmaceutical industries because it acts as a demulcent and emollient. This gum as well as that of psyllium and quince gum may be substituted for tragacanth, gum arabic, etc., in certain operations.

The flax plant is botanically known as "*Linum usitatissimum.*" Botanists are familiar with one hundred species of the plant, but of all these, the only one possessing industrial importance, and the only one readily cultivated is the *Linum usitatissimum.* Flaxseed is cultivated primarily as a source of linseed oil, which is a requisite in the paint and varnish industries. Only a small percentage of the total supply is utilized as a gum source.

The flax plant is extensively cultivated in Argentina, Canada, China, India, Morocco, Russia, and the United States. In the United States, seed-flax is grown chiefly in North and South Dakota, Minnesota, and Montana, but some is produced in Iowa, Missouri, Nebraska, and Wisconsin. During recent years the production of the seed has varied from 17 to 31 million bushels per year.[22] Since 1908 the domestic production of seed has not been sufficient to meet the requirements of our industries, and the deficiencies have been met by importations chiefly from Canada, India, and Argentina.

[21] B. W. Rowland, Research associate, The Institute of Paper Chemistry, Appleton, Wis. Reprinted from Southern Pulp & Paper Journal, 7, No. 7:20-24 (Dec. 15, 1945).

[22] G. S. Jamieson, "Vegetable Fats and Oils," p. 231, The Chemical Catalog Co., New York, 1932.

In the Argentine Republic,[23] the greatest flax growing country in the world, the plant is grown only for the seed although elsewhere the plant fibers are the source of linen.

The flax plant is annual in growth, and rather delicate in structure. It grows from 1 to 4 ft. in height; the stem is slender, branching only slightly at the top, and bears marked, alternate leaves. The flower is mostly sky-blue, though sometimes white. In regions of little rain, the flax is grown primarily for its seed. The growing of the flax crop is very exhausting to the soil; potash and phosphoric acid are the chief ingredients that the soil requires to produce a good crop of flax for either the seed or the fiber. The flax plant is allowed to ripen fully before harvesting, and the flax straw is burned to get rid of it. The plant is then dried and threshed.

The flaxseed[24] is ovoid or oblong-lanceolate, flattened and obliquely pointed at one end. Its length ranges from 4 to 6 mm. It is brown to dusky red externally, and smooth and glossy. Internally, its color is light yellowish to brown to weak yellow and oily. The odor of the seed is slight; taste mucilaginous, oily and distinctive. The spermoderm consists of an epidermis with a mucilaginous outer wall covered by a thin, more or less broken sheath of cutin.

Jaretzky and Ulbrich[25] found that the mucilage in the epidermis cells of flaxseed is formed from the starch and deposited as a mucilage membrane on the primary membrane. In this transformation of starch into mucilage, two different processes can be distinguished: (a) change of the starch into an intermediate with no change in the starch structure; (b) fusion of this intermediate product into mucilage. In this fusion process, the plasmatic structures, which are formed through the condensation of the plasma and fusion of the chondriosomes, play a part. In the metamorphosis of the starch grains into mucilage, the nucleus is a factor. By measurements of nuclei, nucleoles, and starch grains in the cells at stages in development, the nucleus and nuclear particles lose volume and substance in the same degree as the formation of the mucilage progresses. The nuclear particle constitutes a collective or storage center for the necessary materials for the working of the cell. These are activated during the mucilage formation and then discarded in the cell plasma.

Anderson and Crowder[26] found that the mucilage on hydrolysis yielded an aldobionic acid consisting of 1 molecule of *d*-galacturonic acid (I) and

[23] J. M. Matthews, "Textile Fibers," 4th Ed., p. 736, John Wiley & Sons, Inc., New York, 1936.
[24] U. S. Pharm., p. 203, 1936.
[25] R. Jaretzky and H. Ulbrich, *Arch. Pharm.*, **272**, 796-811 (1934).
[26] E. Anderson and J. A. Crowder, *J. Am. Chem. Soc.*, **52**, 3711-5 (1930).

1 molecule of *l*-rhamnose (II). Niemann and Link[27] have confirmed this. Anderson and Crowder state that the molecule is joined together by a glucoside linkage involving the aldehyde group of (I) and an alcohol group of (II). This mucilage is similar in composition and structure to some of the plant gums.

Anderson[28] prepared and purified *l*-galactose from flaxseed directly and from flaxseed mucilage. He found that the mucilage contains 11 per cent of *l*-galactose and that none of the *d*-form is present.

Bailey[29] found that the noncellulosic mucilage of flaxseed is a heterogeneous polysaccharide system capable of fractionation.

The influence of salts on the viscosity of flaxseed mucilage was investigated by Dunnin and Shemyakin.[30] The aqueous solution of the mucilaginous material from flaxseed hulls has a high viscosity—relative viscosity 3.20 in 0.16 per cent solution. They found that the viscosity decreased upon the addition of sodium chloride, potassium chloride, calcium chloride, sodium sulfate, potassium sulfate, sodium nitrate, and potassium nitrate in concentrations from 0.04 to 0.2 *N*. Magnesium sulfate decreased the viscosity in concentration from 0.001 to 0.1 *N* and increases it slowly at higher concentrations. Potassium sulfate, ammonium sulfate, zinc sulfate, and calcium chloride exhibit the rise in viscosity at higher concentrations less markedly than magnesium sulfate. The special behavior of magnesium sulfate is attributed to the influence of magnesium on the swelling of plant colloids.

White flowered flaxseed had the analysis[31]:

Water	6.97%
Ash	3.84
Protein	22.75
Ether extract	30.23
Fiber	5.67
Carbohydrates	30.54

Coumou[32] states that liquids have a structural viscosity if the rate of flow in capillaries is not proportional to the pressure and the viscosity decreases with pressure. Coumou used the Hess viscosimeter in determining the structural viscosity of several solutions. Gelatin solutions (0.7 per cent) show structural viscosity as does a 4 per cent starch solution provided the solution has not been heated more than 2 hours at 122°; after 20 minutes at 155° there is no longer any structural viscosity.

[27] C. Niemann and K. P. Link, *J. Biol. Chem.*, **104**, 205-6 (1934).
[28] E. Anderson, *J. Biol. Chem.*, **100**, 249-53 (1933).
[29] K. Bailey, *Biochem. J.*, **29**, 2477-85 (1935).
[30] M. S. Dunnin and F. M. Shemyakin, *Kolloid-Z.*, **45**, 146-52 (1928).
[31] Analyses of Rhodesian foodstuffs. Division of Chemistry, *Rhodesia Agr. J.*, **31**, 651-8 (1934).
[32] J. Coumou, *Chem. Weekblad.*, **32**, 426-9 (1935).

Dextrin shows a slight structural viscosity while sucrose or glucose solutions do not. Locust bean solution (0.5 per cent), tragacanth (0.5 per cent), and linseed mucilage show structural viscosities, while gum arabic (20 per cent) and cashew gum (30 per cent) do not. Coumou concludes that structural viscosity is found only in solutions containing long stretched particles of a minute size.

Pressure steam extraction of mucilage from flaxseed has been suggested.[33] The seeds are extracted with wet steam under superatmospheric pressure in a closed vessel and the resulting liquid extract is passed to a receptacle under a substantially lower pressure.

Tests carried out by Courdurier[34] on marine fire tube boilers fed with sea water showed that linseed mucilage prevents scale formation, and in time removes scale already formed even with pressures up to 160 lb. per sq. in. The boiler water was not acid to litmus. The Kobzeff apparatus continually prepares the infusion and delivers it to the boiler. Results with water tube boilers were not satisfactory according to Courdurier.

Flaxseed gum after hydrolysis appears to be composed of an aldobionic acid consisting of 1 molecule of *d*-galacturonic acid and 1 molecule of *l*-rhamnose. Its chemical structure closely resembles that of psyllium and quince gum insofar as the polysaccharides are concerned.

Psyllium Seed

Although there is little recorded in the literature, several of the species of *Plantago psyllium* were of economic value before botanical history began to appear in printed form. The psyllium seed is of present commercial interest because its gum is readily dispersed in water, it acts as a thickener, and possesses colloidal properties.

The gum or mucilage of psyllium seed is substituted in some instances for gum arabic, tragacanth, etc., in dye printing.

Psyllium seed is obtained from an annual plant[35] *Plantago psyllium*, which is 8 in. in height. The leaves are linear and narrow, and 1½ in. in length, and its flower is ovoid and ½ in. long. The plant grows freely in dry, sandy soil, and the surface of the plant is sticky due to minute glandular hair.

It is cultivated in the Mediterranean region extending to India. Two crops are raised a year with a yield of 7,000 to 8,000 lb. per acre. After maturity the whole plant is harvested, dried, and threshed similar to wheat.

[33] J. F. Sanftleben (assignor to Filtrators Co., a partnership), U. S. Patent 1,841,763 (Jan. 19, 1932).
[34] Courdurier, *Chaleur & industrie*, **5**, 325-9 (1924).
[35] *Bull. Misc. Inform.*, Roy. Botan. Gardens, Kew, England (1931).

The United States annual imports are greater than 2,000,000 lb. of psyllium seed.[36]

The mucilage or gum from the psyllium seed is utilized in the sizing of silk, printing of fabrics, the manufacture of paper, and as a medicine. In Hindustani[37] psyllium seed, *Plantago ovata* or Isabghol is used chiefly in chronic diarrhea and dysentery, especially in the particular form of intestinal irritation known as "hill-diarrhea."

Plantago or psyllium is the ripe seed of *Psyllium Linné*[38] or of *Plantago arenaria,* known in commerce as Spanish or French psyllium seed. *Plantago ovata Forskal* is known as Blonde psyllium or Indian Plantago seed. Other names designating this seed are: fleawort, flea seed, Plantago plantain and Isabghol.

Plantago psyllium seeds are ovate to ovate-elongate shaped and concavo convex. The length of the seed ranges from 1.3 mm. to 2.7 mm., and rarely reaches 3 mm. The width varies from 0.6 to 1.1 mm. The seeds are light brown to chestnut brown in color, and dark brown along the margin. The seed surface is very glossy.

The seeds of *Plantago arenaria* are ovate to oblong to elliptical in shape and also concave to convex. The length ranges from 1.6 to 3.0 mm., the width from 1.0 to 1.5 mm. The external color is maroon to dark brown. Surfaces are occasionally somewhat glossy, though often dull and rough.

The seeds of *Plantago ovata* are broadly elliptical to ovate and boat shaped. The length varies from 2 to 2.5 mm., and the width from 1 to 1.5 mm. The colors are pale grayish brown with a pink tinge. The surface is dull. The seed coat has a colorless epidermis of cells containing mucilage. These outer walls break down to form layers of mucilage when brought into contact with water.

Examination of the several varieties of psyllium seeds on the United States market gave the following mucilage contents:[39]

French psyllium	11.8%
Blonde psyllium	30.9
German psyllium	11.5

Research on the chemical composition of psyllium seed by Hepburn and Laughlin[40] gave the following percentage compositions:

[36] A. F. Hill, "Economic Botany," McGraw-Hill Book Company, Inc., New York, 1936.
[37] G. P. Pendse and S. Dutt, *Proc. Acad. Sci.* (United Provinces Agra. Oudh, India), **4**, 133-40 (1934).
[38] "The National Formulary," 6th Ed., p. 295, American Pharmaceutical Association, Washington, D. C., 1935.
[39] H. W. Youngken, *J. Am. Pharm. Assoc.*, **21**, 1265-73 (1932).
[40] J. S. Hepburn and T. L. Laughlin, Jr., *Am. J. Pharm.*, **102**, 565-8 (1930).

Composition	Percentage
Total solids	91.50
Moisture	8.50
Crude fat	6.40
Total ash	3.16
Insoluble ash	2.95
Soluble ash	0.21
Crude proteins	17.83
Crude fiber	11.50
Nitrogen-free extractives	52.61
Pentosans	9.85
Galactans	0.31

Alkalinity of soluble ash was such that 6.48 cc. of a *N* acid was required to neutralize the ash yielded by 100 g. of total solids. Alkalinity of insoluble ash required 41.72 cc. of a *N* acid to neutralize the ash yielded by 100 g. of total solids.

Reducing sugars were not present in the psyllium seed. The crude gum was found to be tasteless and odorless and contained 16.45 per cent pentosan and 0.02 per cent galactan.

Pendse[41] stated that the oil content of the seeds of Plantago ovata was 11.42 per cent. This oil contains both saturated and unsaturated fatty acids, the saturated acids being 12.43 per cent of the total fatty acids. In turn these saturated acids are composed of 32.77 palmitic, 60.37 stearic, and 6.80 per cent of lignoceric acids.

Psyllium seeds from Cyprus[42] were found to compare favorably with commercial Spanish and French seeds on the basis of swelling factors of 14.0 to 17.5 per cent and oil content of 6.4 to 7.0 per cent.

Anderson and Fireman[43] found that mucilage from the psyllium seed is a mixture of polyuronides. Its composition is directly dependent on the method of preparation. They found that polyuronides containing the highest amount of uronic acids dissolve the most readily. Heating the mucilage for 20 hr. with 4 per cent sulfuric acid gave a compound of 4-galacturonic acid with 2-arabinose, together with 75 to 90 per cent of gum sugar which was found to be almost entirely *d*-xylose. There are, therefore, 7 to 35 molecules of xylose per molecule of the uronic acid-sugar compound. From 1.5 to 2.5 per cent of an unidentified insoluble compound was also found in the gum.

A study of the chemical composition of whole blonde psyllium seed was made by Hansche and Still[44] as shown in Table 19.

Pendse and Dutt[45] did not find any alkaloidal or glucosidal content of

[41] G. P. Pendse, *Proc. Nat'l. Acad. Sci.* (India), **7**, 137-9 (1937).
[42] Anon., *Cyprus Agr. J.*, **29**, 98-9 (1934).
[43] E. Anderson and M. Fireman, *J. Biol. Chem.*, **109**, 437-43 (1935).
[44] R. Hansche and E. U. Still, *Am. J. Pharm.*, **105**, 433-5 (1933).
[45] G. P. Pendse and S. Dutt, *Proc. Acad. Sci.*, (United Provinces Agra Oudh, India), **4**, 133-40 (1934).

Table 19. Composition of Blonde Psyllium Seed

	Psyllium Seeds %	Hulls %	Gum from Hulls %
Moisture	7.50	—	—
Ash	3.00	2.53	2.53
Total nitrogen	2.30	0.44	0.125
Total phosphorus	0.438	0.102	1.43
Lipoid	8.36	—	—
Pentose	12.30	38.60	83.05

Plantago ovata or Isabghol. The seeds contained 5 per cent of a pale yellow semi-drying oil, a large amount of mucilaginous material, and inorganic ash and reducing sugars.

Nelson and Percival[46] found that *Plantago arenaria* seeds gave 50 g. of mucilage with 5.4 per cent ash after the extraction and precipitation of 1 kg. of the seeds. Precipitation with alcohol containing 50 cc. of concentrated acid per liter gave a product (I) with an acid equivalent of 2,000, 7.5 per cent uronic anhydride, 90 per cent pentosan, and 0.6 per cent ash. Hydrolysis of (I) with 3 per cent oxalic acid gave an 87 per cent mixture of sugars. These sugars are said to contain 9.5 per cent 2-arabinose and 3 per cent *d*-glucose, the remainder being *d*-xylose together with 12 per cent of an aldobionic acid. They found this acid to be composed of *d*-xylose and *d*-galacturonic acid. Product (I) with acetic acid and pyridine yielded an acetate $[\alpha]_D^{17} - 61°$ (chloroform, *c* 0.7). The methyl derivative (II) has $[\alpha]_D^{17} - 104°$ (chloroform, *c* 0.3). Hydrolysis of (II) gave 29.5 per cent trimethylxylopyranose (III), 23 per cent of 2-methylxylose (IV), 4 per cent of tetramethylgalactopyranose (V), and about 40 per cent of a mixture (VI). This mixture is said to be composed chiefly of 3,4-dimethylxylose (VII), but probably containing methylated arabinose in addition. From the amount of (V), tetramethylgalactopyranose, it would seem that all of the galactose in (I) is accounted for by galactopyranose end groups. Product (VI) yields δ-lactone and product (IV) forms an anilide.

The crystalline β-methylxyluside of (VII) and its ρ-toluenesulfonate could not be isolated. An approximate composition by Nelson and Percival of the chemical units gives 9 xylopyranose and 1 galactopyranose end groups, 10 xylopyranose linking units, 8 xylose residues, free HO groups on C_2 at the branching points of the structure, and 2 galacturonic acid residues. These appear to form a more stable union with xylose than with galactose or arabinose.

Anderson, Gillette and Seeley[47] experimented on Indian wheat and

[46] W. A. G. Nelson, E. C. V. Percival, *J. Chem. Soc.*, 58-61 (1942).
[47] E. Anderson, L. A. Gillette, and M. G. Seeley, *J. Biol. Chem.*, 140, 569-74 (1941).

found it contained 19 per cent mucilage which is a mixture of acids varying from approximately 8 to 17 pentosan molecules combined with 1 molecule of *d*-galacturonic acid. The mixture consists of salts of *d*-galacturonic acid combined by a glucoside union from its CHO group with a chain of a few molecules of *l*-arabinose. The latter sugar is attached to a longer chain of *d*-xylose molecules. The *d*-xylose is attached apparently to a small amount of some material which remains as an insoluble precipitate when the mucilage is hydrolyzed. They state that "the mucilage is very similar to that isolated from *Plantago psyllium Linné.*"

Hepburn and Laughlin[48] tested the gum of psyllium seed with several solutions, as given in Table 20.

Table 20. Action of Reagents on Psyllium Extract

Testing Solutions	*Results*
Lead subacetate	Curdy precipitate
Ferric chloride (25 per cent)	Marked darkening
(The addition of 15 cc. of 50 per cent alcohol caused the color to disappear and no precipitate was formed)	
Copper sulfate	Transient mahogany color
(Further addition of an excess of 5 cc. of 5 per cent sodium hydroxide gave a flocculent bluish-green precipitate which did not dissolve on boiling)	
Potassium hydroxide (5 per cent)	Yellow froth
Lugol's iodine (drops)	No change except for color due to presence of iodine
(Hepburn and Laughlin state starch and erythrodextrins are not present)	
Alcohol (95 per cent)	Faint turbidity, then flocculent precipitate
Hydrochloric acid (36 per cent)	Darkened, purple tinge
Sulfuric acid	Caramel odor
Phosphoric acid	Darkening of color and fragrant odor
(Fehling's solution was not reduced)	
Lead acetate (10 per cent)	Flocculent, slimy pale yellow-green precipitate

Gutbier, Huber and Eckert[49] showed that the mucilage from *Plantago psyllium* seeds can be utilized as a protective colloid. The colloid is prepared by washing the seeds with cold water saturated with chloroform. The seeds are extracted with water plus chloroform at 25°, 50°, 75° and 100°C. about 6 hr. The resulting solutions are slightly yellow to amber colored. Its electrical character is slightly negative. Alkalies stabilize the extract and acids precipitate it. They state that "Colloidal selenium prepared with 0.2 to 0.3 per cent of the mucilage as protective colloid is very stable and practically fully reversible." Pouring such a solution into absolute alcohol gives a fully reversible residue which is slightly thermosensitive.

Another colloidal solution can be prepared by adding dilute hydrazine hydrate drop by drop to 100 cc. of mucilage solution containing 1 cc. of

[48] J. S. Hepburn and T. L. Laughlin, Jr., *Am. J. Pharm.*, 102, 565-8 (1930).
[49] A. Gutbier, I. Huber, and P. Eckert, *Kolloid-Z.*, 32, 255-62 (1923).

telluric acid. According to Gutbier, Huber and Eckert concentrations higher than 0.3 per cent of the protective colloid are not stable, the electrical character is negative, and these dried colloids or those dehydrated with alcohol are all irreversible.

The purification of the gum from *Plantago psyllium* seed is suggested in a process[50] in which the mucilage is first extracted with boiling water until the mucilage present has swelled. The dispersed mucilage is then separated from the cellulose and other portions of the material by gravity under conditions of low viscosity. This is accomplished by diluting with water containing agar dispersed in it. This serves to reduce the stickiness of the dispersed mucilage and facilitates separation so that a top clean layer of mucilage and dispersed agar is formed.

Pectins and mucilages contained in plantain seeds are extracted with water in a closed vessel at a temperature above 100°C., according to Olivier.[51]

Studies of many investigators indicate agreement that the gum of psyllium seed is readily extracted with boiling water. The composition of the gum depends on the method of preparation. Heating the gum with sulfuric acid produces a compound made up of galacturonic acid with 2-arabinose and a gum sugar which is almost entirely *d*-xylose. Precipitation of the gum with hydrochloric acid gives a product composed of uronic anhydride and pentosans. Hydrolysis of this product gives a mixture of sugars containing 2-arabinose, *d*-glucose, *d*-xylose, and aldobionic acid composed of *d*-xylose and *d*-galacturonic acid. By virtue of its chemical structure, psyllium seed gum appears to be related to the celluloses and the sugars.

Quince Seed

Quince seed gum is of commercial interest because it is water soluble, acts as a stabilizer and thickener, and has demulcent properties.

The quince was known as "the golden fruit" in the early history of Greece and in biblical times. It is a native of the Near East, and is cultivated in southern Asia, Europe, South Africa and America.

The principal source of quince seed is Iran (Persia), although lesser quantities are also imported from Iraq, Portugal and the Union of South Africa. Imports from Iran (Persia) and the total imports of quince seed for the years 1939 to 1942 inclusive are given in Table 21.[52]

The 1940 census of the Department of Agriculture indicates that the

[50] H. B. Near, A. J. Pacini, R. W. Crosley, M. M. Gerth, F. T. Breidigam and J. D. Kelly, U. S. Patent 2,010,880 (assignors to Libby, McNeill & Libby) (Aug. 13, 1935).

[51] H. Olivier, French Patent 694,460 (July 27, 1929).

[52] U. S. Dept. of Commerce, Bureau of Census, Washington, D. C.

United States produced 63,869 bushels in 1939. The principal quince growing states were New York, Michigan, Pennsylvania, and Maryland.

The American quince is primarily utilized as a canned fruit or in the manufacture of jellies or preserves.

The Persian quince seed is said to contain the most mucilage. Although there is no data published concerning the extraction of the seed from the fruit, it is believed that the fruit is cut in half and dried in the

Table 21. Quince Seed Imports

	1939	1940	1941	1942
Total imports:				
Pounds	129,208	189,709	221,616	154,131
Dollars	$ 62,276.	$141,892.	$274,904.	$150,198.
Imports from Iran:				
Pounds	113,117	152,759	161,409	141,189
Dollars	$ 61,118.	$116,771.	$197,342.	$144,068.

sun. The dried seeds are shipped directly to the importers who in turn sell them directly to the cosmetic and pharmaceutical firms.

The mucilage from the quince seed is used extensively in the cosmetic industry as a demulcent agent in hand lotions, hair waving and cleansing lotions, and in medicinal preparations.

The source of the quince[53] is a small, shallow rooted tree of the order of *Rosaceae* and allied to the Pyrus. Its leaf, flowers, and fruit closely resemble those of the apple and pear tree. The fruit is a yellow pome which is covered with wooly hair when in an unripe condition. These loosen and mostly fall off as the fruit matures. Like the apple[54] each fruit possesses five ripened carpels which constitute a core, and each of these contain six to fifteen seeds arranged in two rows.

Quince seeds,[55] *Cydonia Vulgaris*, are egg shaped, angled, and reddish-brown in color. The seeds are white within, inodorous and nearly insipid, and are surrounded by a leather-like membrane abounding in mucilage.

Lathrop and Walde[56] state that the seeds of the Japanese quince are not as slimy or mucilaginous as the European quince. The carpels are large and abundantly filled, and contain twenty seeds per cell and at least fifty seeds per fruit.

Analysis of two samples of quince seed, Swiss and foreign, by Pritzker and Jungkunz[57] gave:

[53] G. Hadary, *Food Industries*, 15, 76-7 (Feb. 1943).
[54] U. S. Dispensatory.
[55] H. Goodman, "Cosmetic Dermatology," p. 142, McGraw-Hill Book Company, Inc., New York, 1936.
[56] C. P. Lathrop and W. L. Walde, *Am. Fruit Grower*, 48, 8 (Apr. 1928).
[57] J. Pritzker and R. Jungkunz, *Pharm. Acta Helv.*, 13, 29-34 (1938).

Ash content	5%
Mucilage	4%

The phosphorus content of the two samples was 25.9 per cent and 26 per cent. Further analysis revealed that no pectin was present in the mucilage and that the ash was strongly basic.

Renfrew and Cretcher[58] hydrolyzed the gum of quince seed with sulfuric acid. The decomposition products found were inorganic salts, about 33 per cent of the cellulosic residue, a small amount of arabinose, and a mixture of aldobionic acids, as well as a mixture composed of methylated and unmethylated hexuronic acids in combination with xylose.

The analytical values of quince seed gum are listed in Table 22.

At the end of the hydrolysis, there remained a bulky residue representing about one-third of the dry weight of the gum. The composition resembled $C_6H_{10}O_5$. On a calculated basis, carbon = 44.47 per cent, hydrogen = 6.17 per cent. The actual carbon and hydrogen found were carbon = 43.78 per cent, and hydrogen 6.44 per cent. About 28 per cent of the residue was removed as α celluloses by the action of 17.5 per cent solution of sodium hydroxide. Most of this was reprecipitated by acetic acid.

When the gum was prepared by precipitation in an acidified solution, it was possible to separate arabinose and a more soluble gum fraction from the concentrated liquors. This more soluble gum contained about 30 per cent uronic acid and 52 per cent pentose.

Table 22. Composition of Quince Seed Extracts

	Acidic Gum	Neutral Gum
Methoxy	3.3%	2.9%
CHO (iodine titration)	1.4	—
Uronic acid (titration with 0.1 N NaOH)	26.1	—
Carbon dioxide	6.0	6.0
Uronic acid (calculated from carbon dioxide)	27.8	26.0
Ash	2.0	6.0
Cellulose	33.0	33.0
Total	95.8	96.0

Studies by Hadary[59] with ice cream showed that mixes containing 10 to 16 per cent fat and stabilized with 0.03 to 0.04 per cent quince seed extract had body properties comparable to ice cream containing 0.3 to 0.4 per cent of 225 Bloom gelatin. At those concentrations, neither gelatin nor quince seed extract showed any decided advantage as far as flavor, body, and texture of the ice cream were concerned. The whipping time of

[58] A. G. Renfrew and L. H. Cretcher, *J. Biol. Chem.*, 97, 503-10 (1932).
[59] G. Hadary, *Food Industries*, 15, 76-7 (Feb. 1943).

the quince stabilizer was slightly shorter than that of the gelatin stabilized mixes.

Quince gum stabilized ice cream mixes attained their maximum viscosity immediately after processing. The addition of 0.010 to 0.025 per cent of quince seed extract in a dry form decreased the viscosity of the mixes as compared to the viscosity of the non-stabilized mixes. Ice cream stabilized with quince seed extract does not melt uniformly as did that stabilized with gelatin. The extract dissolves readily in the ice cream mix at from 45 to 190°F. and lends itself to homogeneous incorporation in the mix. Because the seed coat is a highly complex combination of cellulose or hemicellulose with a polysaccharide that yields arabinose and xylose on hydrolysis, it is devoid of toxic properties.

Hadary found that the neutral gum contained:

Ash	6%
Silicon oxide	25
R_2O	15
Calcium oxide	16
Magnesium oxide	8
(with considerable amount of phosphate)	

Hadary also found that the gum of quince seed is effective as a stabilizer in dairy products. Milk containing 0.03 per cent to 0.04 per cent of the extract mixed with 10 parts by volume gave a non-settling chocolate milk.

Kirchner and Tollens[60] describe a process for the purification of quince seed mucilage, which consists of precipitating the gum by the addition of alcohol, after hydrochloric acid has been added. This is repeated six or eight times. The product obtained is repeatedly washed with absolute alcohol, and finally ether. In this manner the ash is reduced to a minimum and the mucilage when dried is obtained as a porous mass, and not hard lumps.

The mucilage was obtained from quince seeds by digesting them in water for four hours, then rubbing them through a hair sieve, boiling and straining through linen. After purification, the mucilage was grayish-white in color, and swelled when soaked in water to form a gelatinous mass. The mucilaginous solution only formed on the addition of a small quantity of potassium hydrate. It still contained 4 to 5 per cent of mineral matter, and on analysis, gave numbers corresponding with the formula $C_{18}H_{28}O_4$. When boiled with dilute sulfuric acid, white flocs were precipitated, and sugar and dextrin or gum were produced. From the results of numerous experiments, it seemed that the flocculent precipitate of cellulose was nearly constant after the first half hour, however long the boiling may be

[60] W. Kirchner and B. Tollens, *Am. J. Pharm.*, **48**, 35 (1876).

continued. The per cent of gum gradually decreased, while that of sugar increases within certain limits, showing the conversion of the former into the latter. The gum when polarized is laevorotary and the sugar which reduces cupric solution is dextrorotary. The flocculent precipitate amounting to about 36 per cent gave the reaction of cellulose with iodine, but on analysis comes out slightly higher than that required by the formula $C_6H_{10}O_5$.

Mucilage from quince seeds is readily extracted with boiling water. The usual procedure is to macerate for one-half hour, 2 parts of quince seed and 100 parts of water in a covered vessel. The mass is agitated frequently and then drained without pressure through muslin.

The U. S. Dispensatory recommends that the mucilage be freshly prepared as needed.

The gum of quince seed appears to be composed of cellulose, *l*-arabinose and xylose. By virtue of its chemical composition, the gum appears to be related to the celluloses and the sugars. It is similar in composition to flaxseed gum and psyllium seed gum.

Iceland Moss

Iceland moss is classified as a hemicellulose; it contains cellulose and the simple sugars. Chemically, it is similar in composition to the other hemicelluloses.

The mucilaginous material or gum extracted from Iceland moss is utilized in cosmetic preparations, and in the sizing of textiles. In the countries where it is grown it finds application as a food for livestock, and its jelly is incorporated in light soups, porridges, and gruels for convalescent patients.

Iceland moss is botanically known as *Cetraria islandica*. It is not in a sense a true moss, but a lichen, and is grown in northern countries. It is commercially exported from Iceland, Sweden, and Norway.

In Iceland[61] it is harvested in a bare, stony soil where no admixture of other vegetation is present. The natives revisit the locality every three years, which is the time required for it to grow to a profitable size. The plant is gathered in the wet season because it is more easily detached when wet. If the weather is dry, they collect it at night.

The moss is cleaned so as to remove any foreign matter present, and washed in water to remove the bitter principle as much as possible. It is then dried and powdered. The cetraric acid in Iceland moss is removed by macerating the powder in water for 24 hours, or soaking with a solution of soda or potassium carbonate.

[61] A. L. Smith, "Lichens," University Press, Cambridge, England, 1921.

Iceland moss is derived[62] from the *Thallus fruticose* whose lobes are comparatively narrow, rolled, rigid, and erect. The margin is lined with a rigid celia. The upper surface is chestnut brown in color, and the lower surface is somewhat lighter. The apothecia is a medium disk, chestnut brown in color, and the spores are typical. Many years ago the brown color obtained from Iceland moss was utilized as a dye for woolen materials.

An analysis of the ash of Iceland moss from Tyrol, by Rosenthaler and Beck[63] revealed that it contained copper, silver, arsenic, tin, nickel, cobalt, zinc, chromium, manganese, aluminum, titanium, iron, calcium, magnesium, lithium, potassium, sodium, ammonium (NH_4), chlorine, bromine, sulfate, phosphate, silicate, and carbonate. Poland moss and Italian moss contained no silver. Yttrium was identified by spectroscopic examination of the oxalate precipitate.

Buston and Chambers[64] found that the cell walls of Iceland moss consist mainly of hemicelluloses and cellulose, and that pectins, pentosans, and lignins were absent.

Granichstädten and Percival[65] extracted 1 kg. of Iceland moss with a 1.5 per cent solution of sodium bicarbonate and 20 times with boiling water, 15 liters each time, for four hours. The residue (366 grams) was dried at 70°/12 mm. and then extracted twice at room temperature with 16.1 liters of a 4 per cent sodium hydroxide solution, and drained through muslin. The filtrate, 8.3 liters, was acidified with acetic acid and precipitated with 9.2 liters of ethyl alcohol. The centrifuged precipitate was dissolved in 5.14 liters of sodium hydroxide, centrifuged, and treated with 1.28 liters of Fehling solution, followed by 5 liters of ethyl alcohol. The copper complex was treated with 11.2 *N* hydrochloric acid and the hemicelluloses were precipitated with 2.5 liters of ethyl alcohol. The precipitate was treated with 4.8 liters of hot, dilute sodium hydroxide, acidified with acetic acid, and 3.44 liters of ethyl alcohol added. This gave 89 per cent of the hemicellulose containing 4.95 per cent uronic acid. The addition of 2.5 liters of ethyl alcohol precipitated the remainder of the hemicelluloses with 8.5 per cent uronic acid. Hydrolysis of the hemicelluloses with 3.7 per cent sulfuric acid for 3.5 hours gave a mixture containing galactose 7.6, mannose 3, glucose 89 per cent. Hydrolysis of the hemicelluloses with 15 per cent sulfuric acid at 100° for 24 hours gave *d*-glucuronic acid. The hemicelluloses were then

[62] A. Schneider, "Guide to the study of lichens," Bradleed Whidden, Boston, Mass, 1898.
[63] L. Rosenthaler and G. Beck, *Pharm. Acta Helv.*, **12**, 94-6 (1937).
[64] H. W. Buston and V. H. Chambers, *Biochem. J.*, **27**, 1691-1702 (1933).
[65] H. Granichstädten and E. G. Percival, *J. Chem. Soc.*, 54-8 (1943).

acetylated and methylated, the product being separated by fractional precipitation from chloroform by petroleum ether into four fractions found in Table 23. Each fraction was subjected to methanolysis, and the bulk of the methylated methyl glucoside in every case was to be found in a middle fraction (80 to 90 per cent of the total distillate) which on complete methylation and hydrolysis yielded tetramethylglucopyranose. The corresponding trimethylglucose, prepared by hydrolysis of this middle fraction, in each case yielded crystalline 2,3,6-trimethylglucose and 8 to 18 per cent of 2,4,6-trimethylglucose anilide, melting at 162 to 166° $[\alpha]_D^{15}$ − 113° (methanol, c 1).

A study of the trimethylglucoses given in Table 24 showed the percentages of the 2,3,4-, 2,3,6-, 2,4,6- and 3,4,6- isomers in each fraction.

Table 23. Iceland Moss Fractions

	Per cent Methoxyl	$[\alpha]_D^{12}$ in Chloroform	$\eta_{sp.}^{25}$	Apparent Molecular Weight
II.	40.5	—	0.428	28,000
III.	43	11°	0.771	51,000
IV.	43	2.5°	0.767	42,000
V.	41	−2°	0.209	12,000

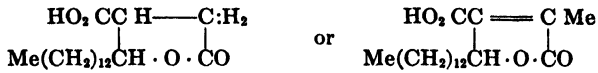
Table 24. Iceland Moss Trimethylglucoses

	Per cent			
II.	31,	30,	25,	14
III.	13,	29,	8,	50
IV.	9,	47,	5,	39
V.	6,	50,	10,	34

Compound II yielded a small amount of tetramethyl-*d*-galactopyranose anilide (3.5 per cent as the methyl glycoside), showing that a non-reducing terminal group of *d*-galactopyranose was present in the fraction. Compound III yielded 2.5 per cent of a fully methylated methyl glucoside, which was a mixture of 2,3,4,6-tetramethyl-*d*-glucose and -*d*-galactose. The hemicellulose fraction must therefore have a branched chain structure with at least 2 branches terminated by *d*-gluco- and *d*-galactopyranose units respectively. It is the authors' opinion that the hemicelluloses are mixtures of polysaccharides made up chiefly of -glucose units linked through positions 1,2; 1,3; 1,4; and 1,6, the first being of a type of linkage not so far reported for glucose units.

Asano[66] isolated from Icelandic moss, of the province of Nikko, an *l*-protolichesteric acid, $C_{19}H_{22}O_4$, melting at 107.5 to 108°, for which he suggested the structure:

[66] M. Asano and T. Kanematsu, *J. Pharm. Soc.* (Japan) **51**, 390-5 (1931) (in German 35).



Using the same method Asano and Kanematsu isolated from Icelandic moss, of the province of Tateyama, a compound (I), melting at 121-2° $[\alpha]_D^{15}$ − 32.06° which did not depress the melting point of *l*-lichesteric acid, $C_{19}H_{32}O_4$, melting at 124°, isolated from Icelandic moss of Nikko. When a 10 per cent solution of sodium hydroxide is added to (I) and heated on a water bath for two hours, lichesteric acid melting at 83 to 84° is obtained. This did not depress the melting point of the lichesteric acid obtained from the Icelandic moss of Nikko. The authors obtained a mixture of equal quantities of *l* and *d*-protolichesteric acid, melting at 107°, from the European Icelandic moss, which melts at 100 to 101°.

Asahina and Yanagita[67] state that the structures established by Asano of protolichesterinic and lichesterinic acid, did not deal with *Cetraria islandica Ach.*, but with a lichen now considered to be an independent species *Cetraria tennifolia* (Retz.). On this basis, the authors undertook a study of the true *Cetraria islandica*. It was gathered on Mt. Asibetu and morphologically is identical in all respects to the European lichen. They found that it contained about 4 per cent of a fatty acid mixture, melting at around 90°, $[\alpha]_D^{20}$ − 45.62° (chloroform), from which *d*-protolichesterinic acid was readily isolated. The mother liquor then yielded a strongly *l*-rotatory isomer, *l*-alloprotolichesterinic acid. When this acid was treated with acetic anhydride *l*-lichesterinic acid was obtained, and a pyrazoline derivative upon the addition of cyanamide (CH_2N_2). Asahina and Yanagita conclude that the pyrazdine derivative must be structurally identical to protolichesterinic acid. The fatty acid mixture was heated with acetic anhydride and gave *l*-lichesterinic acid.

The fumarprotectraric acid which is always found in the European *Cetraria islandica Ach.*, could not be detected in the Japanese *Cetraria islandica Ach.*

Kpfler and Ratz[68] state that the crystals arising from the microsublimation of *Cetraria islandica* consist according to the micro melting point determination not of lichesterolic acid, as heretofore given in the literature, but of fumaric acid.

Rielly, Hayes, and Drumm[69] prepared lichenin from Iceland moss and purified it through the acetate. Upon the addition to a mixture of 3 parts by weight of sulfuric acid and 1 part by weight of nitric acid at room temperature, a pentanitrate resulted. In its general reactions, this appeared

[67] Y. Asahina and M. Yanagita, *Ber.* **69B**, 120-5 (1936).
[68] L. Kpfler and H. Ratz, *Arch. Pharm.*, **270**, 338-40 (1932).
[69] J. Rielly, M. Hayes, and P. J. Drumm, *Proc. Roy. Irish Acad.*, **40B**, 102-5 (1931).

to be very similar to the corresponding cellulose nitrate. When the pentanitrate was gelatinized with a solvent, it gave a product resembling horn.

Proner[70] found that in nearly every case if a section of Iceland moss is immersed for 2 to 3 minutes in a 25 per cent solution of ammonia, a rose-red to red color developed in the central hyphae, which changed to a brownish-red color on treatment with ferric chloride.

Leclerc[71] found that cetrarin found in *Cetraria islandica L* would cause the flow of bile and pancreatic juices and peristaltic contraction of the esophagus and stomach when injected intravenously.

F. Ohl[72] points out that sizing agents can be detected on rayon and staple rayon by soaking a 20 g. sample in 500 cc. of distilled water at 60° for four hours. The solution is then poured off and the sample washed with 200 cc. of distilled water. The solutions are combined, filtered, and evaporated nearly to dryness. In the hot water extract the presence of Iceland moss may be detected because it gives a flocculent, jelly-like precipitate with ethyl alcohol.

About 60 per cent of Iceland moss dissolves when boiled with water containing a little sodium bicarbonate. The solution forms a jelly when cold. Carbohydrates including lichenin are extracted with cold water.[73]

Iceland moss when boiled after the removal of cetraric acid, yields a jelly which forms the basis for light soups that are easily digested, or combined with milk. It is considered as a valuable product for those who suffer with a dyspeptic condition.

Northern nations[74] pulverize the moss and incorporate it in breads, gruels, etc. Considerable quantities have been used in the manufacture of sea biscuits, which are said to be less liable to the attack of weevils than where only wheat flour is used.

The gum of Iceland moss is utilized for the preparation of materials suitable for the care of the skin and hair, just as are the gums from Irish moss, quince seed, psyllium seed, etc. The gum is water soluble and readily extracted.

By virtue of its chemical structure, it appears to be a hemicellulose, containing uronic acid, galactose, mannose, and glucose.

[70] M. Proner, *Pharm. Zentralhalle*, **72**, 227 (1931).
[71] H. Leclerc, *Presse méd.*, **42**, 1692 (1934).
[72] F. Ohl, *Kunstseide u. Zellwolle*, **20**, 230-1 (1938).
[73] S. R. Trotman, *Chem. Trade J.*, **82**, 601-2 (1928).
[74] A. L. Smith, "Lichens," University Press, Cambridge, England, 1921.

Chapter 8

The Modified Celluloses

Cellulose is insoluble in water and does not show properties of swelling in the same sense as do the gums. When treated with alkyl halides such as methyl chloride or alkyl sulfates after a preliminary chemical treatment, they may be converted into cellulose ethers. A number of these cellulose ethers have been prepared and some of them are available in commercial quantities.

The lower methylated celluloses are soluble in cold water but in contrast to the gums are insoluble in hot water, and are precipitated out of solution when the temperature is raised sufficiently high or to boiling. With increase in methoxy content the water solubility diminishes until complete water insolubility is reached. In addition, the solubility of the water-soluble methyl celluloses may be greatly decreased by treatment with an aldehyde such as formaldehyde. Methyl cellulose has been suggested as a thickener or a mechanism for increase of viscosity for textile printing pastes in competition with modified starches, dextrins, and the gums. It is very sensitive to alkalies. It has been introduced into the textile industry earlier under the trade name of Colloresine.

Colloresine is described by Knecht and Fothergill[1] as a loose, fibrous material that looks like cotton.

Colloresine D.K. of differing methoxy content has about double the thickening power of the "D" form. It swells quickly in warm water and finally dissolves completely when stirred. It is insoluble in hot water and in alkaline solution so that a solution on heating precipitates, but on cooling dissolves. During treatments with steam or hot solutions to which the printed goods are subjected for development and fixation of the colors, the printing colors thickened with Colloresine D.K. do not "mark off" or "bleed," for the gum is insolubilized by the heat. Later the thickening is removed by washing in cold water.

Ammonia and dilute caustic soda do not affect the thickening; potassium and ammonium sulfocyanides, organic acids such as acetic, lactic or tartaric acid, glycerine, alcohol and certain other organic substances pro-

[1] E. Knecht and J. B. Fothergill, "The Principles and Practice of Textile Printing," 3rd Ed., pp. 138-9, Charles Griffin & Co., Ltd., London, 1936.

mote swelling and improve the body and viscosity of Colloresine solutions; while addition of concentrated alkali carbonates and caustic soda, phenols, tannic acid and neutral or basic metallic salts cause Colloresine thickenings to settle out in flakes. Colloresine thickenings do not become moldy, sour or water. They may be mixed in any proportion with other vegetable thickenings ordinarily used.

Knecht and Fothergill state that "Colloresine is unsuitable for printing dyestuffs and all printing mixtures of a strongly alkaline nature, such as those employed in the usual processes for printing of vat colors." It permits the delay for long periods before development of vat colors after printing. Colloresine permits use of printing colors free from alkali, in that way preventing impairment to printing blankets, copper rollers, felted blocks, brushes and other accessories. In printing of chrome mordant colors and of the insoluble azo-colors produced on the fiber, the cloth after washing is softer and of better feel than obtainable when gum or starch thickenings are used.

Methyl cellulose of American manufacture is produced in six viscosity types to meet a wide range of use requirements. These are listed in Table 25, and each type is identified by a number which corresponds to the average viscosity in centipoises at 20°C. of its 2 per cent solution in water. The viscosity limits within which each type is furnished are also shown in Table 25.

Table 25. Methyl Cellulose Viscosity Types

Absolute Viscosity of 2% Aqueous Solutions at 20°C.		
Viscosity Type	Viscosity of 2% Solution—Centipoises	
	Average	Limits
15 cps.	15	14-18
25 cps.	25	20-30
100 cps.	100	90-150
400 cps.	400	350-550
1500 cps.	1500	1200-1800
4000 cps.	4000	3000-5000

For use as a thickener, the 1500 cps. or 4000 cps. types of methyl cellulose are most economical, but for applications requiring only protective colloid action the lower viscosity types are preferred. Methyl cellulose is a synthetic cellulose ether produced under chemical control of raw materials and reaction product. Reproducible results are more likely in contrast to natural gums whose quality is subject to the vagaries of nature. Methyl cellulose is free from insoluble substances or extraneous matter and generally requires no further processing or filtering before use.

Dispersions of only 1 to 2 per cent concentration of the 4000 cps. type are highly viscous.

Methyl cellulose usually contains only about 0.1 per cent ash and 3 per cent moisture, whereas most water-soluble gums run from 3 to 6 per cent ash and 7 to 10 per cent moisture, as Table 26 shows.

Methyl cellulose is stable to heat, light and ageing. Solutions retain their viscosity on standing over a wide range of pH conditions and ordinarily do not require a preservative.

Methyl cellulose is neutral, odorless, tasteless and inert. It produces clear, colorless aqueous solutions. In contrast, the natural gums tend to give turbid solutions and usually have an acid reaction. The acid values of several of the more commonly used gums are given in Table 26 for comparison.

Table 26. Acid Number of Natural Gums and Methyl Cellulose

	Acid Number[1]	Percent Ash	Percent Moisture
Methyl cellulose—All viscosity types	Neutral	0.2	5.0
Arabic (Acacia)—U.S.P. Powder	2.5	2.72	10.2
Carrageen (Irish Moss or Chondrus)—N. F. Powder	Alkaline	21.08	10.0
Ghatti	2.2	2.73	11.8
Karaya—No. 1, Powdered	25.5	5.52	10.3
Locust Bean—Powder, No. 175 Mesh	4.2	0.97	9.62
Quince Seed	2.2	4.12	7.52
Tragacanth—No. 1 White Ribbon	2.0	2.08	6.74

[1] The acid number is expressed as the milligrams of KOH required to neutralize 1 g. of the gum.

Methyl cellulose is soluble in cold water down to freezing temperatures. Heat will create cloudiness in dilute solutions or produce coagulation in more concentrated dispersions but upon cooling, the colloid will again assume its original clear smooth appearance. This process may be carried out repeatedly without resultant harm to the solution or jelly.

Methyl cellulose is insoluble in most of the common organic solvents. Certain solvents exert a swelling or dispersing action; among these are phenol, cresol, formamide, formic acid, phenyl ethyl alcohol, and beta-phenoxy ethanol.

Aqueous methyl cellulose dispersions are compatible with most water-miscible organic solvents. Water solutions can be diluted infinitely with alcohol without precipitation.

Dry methyl cellulose will not disperse in an aqueous alcohol mixture containing in excess of 40 per cent alcohol. Methyl cellulose must be first dissolved in water and the water-miscible material be then added. Stable dispersions can be frequently prepared in this manner.

Methyl cellulose solutions will tolerate large quantities of univalent ions such as thiocyanates, iodides, bromides and chlorides but smaller amounts of polyvalent ions such as carbonate, sulfate or phosphate will cause precipitation. Methyl cellulose solutions are coagulated by tannic acid, phosphotungstic acid, sodium formaldehyde sulfoxylate, and certain direct dyestuffs. Methyl cellulose solutions are compatible with fast color salts and with most acid dyestuffs.

Methyl cellulose is compatible with dilute acids, alkalies, most water-soluble resins and wetting agents. A pH range of 2 to 12 will cause no apparent change in solution viscosity, color, solubility, or surface tension properties of the solution.

Methyl cellulose forms jellies, pastes and solutions only in cold water. It does not dissolve or disperse to any practical extent when the water is hot.

Methyl cellulose is wet out easily by first mixing the material thoroughly with approximately half the required water at boiling temperature, and allowing it to soak for twenty to thirty minutes with agitation. The remaining water may then be added either as cold water or as ice. The mixture should then be cooled to room temperature and stirred until smooth. Methyl cellulose solutions of maximum clarity may be obtained by reducing the temperature to 5°C. to 10°C. during the cooling period.

Methyl cellulose solutions may also be prepared simply by stirring in water at room temperature. The initial hot water treatment, however, hastens dispersion and prevents the formation of gel lumps. Cooling to 5°C. to 10°C. insures the preparation of haze-free, colorless solutions.

Methyl cellulose as a thickening agent is compared with some of the natural gums by the curves of Fig. 41. The viscosity designation in centipoises on the left-hand vertical scale indicates the relative amount of body derived from the thickening agent at any concentration from 1 to 8 per cent by weight. The scale comprises a range of 1 to 100,000 centipoises. A viscosity of one centipoise is the approximate viscosity of pure water at 20°C. while viscosities of much more than 100,000 centipoises are practically impossible to determine by flow methods since they are beginning to approach a semi-solid state.

The curves show that a smaller concentration of the 4000 cps. type of methyl cellulose is required to produce a solution of a given viscosity than any other viscosity type of methyl cellulose. The lower viscosity types of methyl cellulose are generally used where a higher content of solids is desired together with a low solution viscosity. For example, a spray coating application would require a low viscosity type material. In general, methyl cellulose of the 1500 or 4000 cps. viscosity type is most useful as a thickening agent.

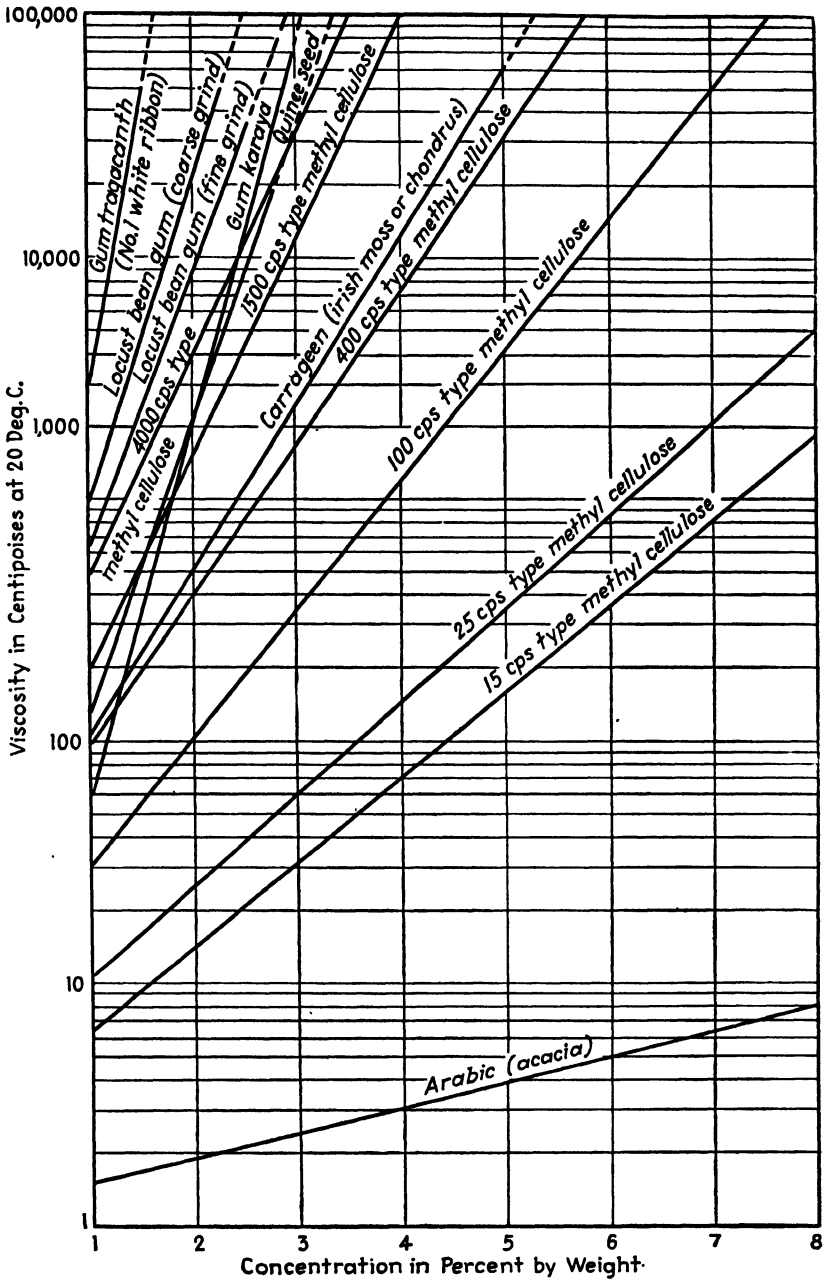


FIGURE 41. Viscosity comparison of methyl cellulose with natural gums.

This chart will prove valuable for determining the approximate amounts of any one of the various viscosity types of methyl cellulose required to match the viscosities produced by the more common water-dispersible natural gums. For example, it would require approximately a 2.5 per cent concentration of 4000 cps. type methyl cellulose to produce a viscosity of 10,000 cps. This same amount of gum karaya or quince seed would also be required since the curves representing these gums also intersect the 10,000 cps. horizontal line at approximately the 2.5 per cent vertical concentration line. Similarly, it will be seen that approximately 1.25 per cent and 1.75 per cent of tragacanth and locust bean respectively will be required to produce the same viscosity. While these curves representing methyl cellulose are characteristic for each type of methyl cellulose and reproducible within the viscosity limit specifications provided (Table 25), it must not be assumed that all other samples of the same kind of gums will give viscosity curves identical to those represented. The viscosity of natural gums varies according to the season of the year they are collected, their length of time in storage and their purity.

The effect of temperature on a methyl cellulose solution is illustrated

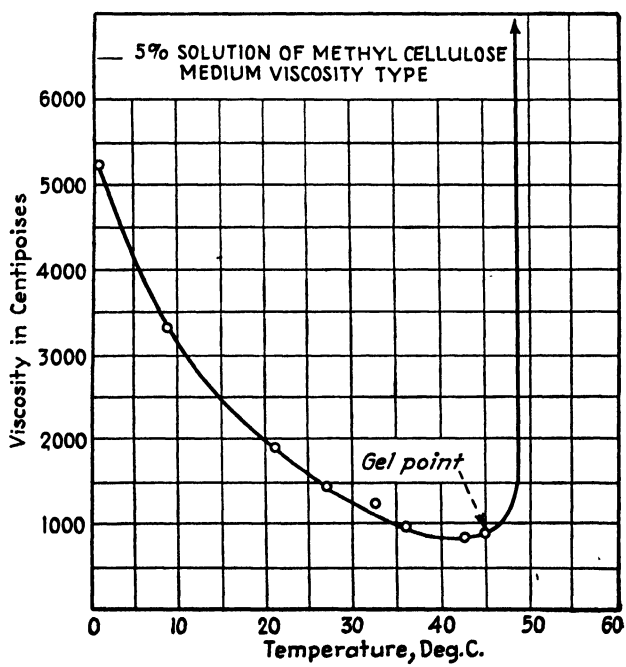


FIGURE 42. Effect of temperature on viscosity of an aqueous methyl cellulose solution.

by the curve of Fig. 42 for a 5 per cent solution of medium viscosity methyl cellulose. When a cold solution of methyl cellulose is warmed, the viscosity decreases as the curve shows. A temperature is eventually reached at which small increases in temperature produce rapid increases in viscosity. Within the range of a very few degrees, the solution transforms to a firm gel. The temperature at which this occurs is the gelation temperature. By lowering the temperature below this point, and stirring, the gel can be returned to the original smooth flowable solution.

The temperature which causes aqueous solutions of methyl cellulose to gel is dependent upon the concentration of methyl cellulose in the solution and upon the viscosity type of methyl cellulose used. In general, the greater the concentration of methyl cellulose, or the higher the viscosity type, the lower will be the temperature at which gelation occurs.

A more specific relation between gelation temperature and concentration for the four viscosity types of methyl cellulose is shown graphically in Fig. 43.

The diagonal lines show the temperatures at which various concentrations of each viscosity type are transformed to gels. The ends of the lines at high temperature indicate concentrations below which the solution will not "set" to a gel regardless of the temperature used. The ends of the lines at lower temperatures indicate concentrations at which the

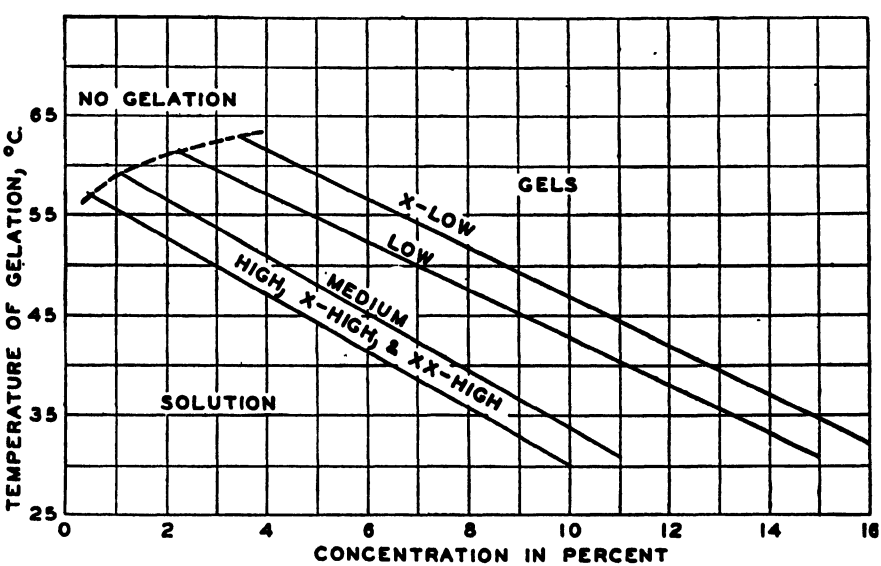


FIGURE 43. Gelation temperature-concentration chart for methyl cellulose viscosity types.

solutions are so viscous that they do not flow. The chart is useful for predicting temperatures below which solutions of the various viscosity types of methyl cellulose will remain fluid.

Carboxymethylcellulose

When cellulose is steeped in alkali metal hydroxide solution (18 per cent caustic for 4 to 6 hr. for example), alkali cellulose is formed. When this alkali cellulose is acted on by monochloracetic acid, there is a conversion to a white, granular, odorless, tasteless powder, designated as carboxymethylcellulose. The sodium salt of this powder is known as sodium carboxymethylcellulose, cellulose gum, sodium cellulose glycolate, trade names such as Carboxy Methocel, Collocel and CMC. This salt is readily soluble or dispersible in water or in alkaline solutions so that thick highly viscous sols are formed whose characteristics differ in degree and chemical properties from those of the water-dispersible proteins, the vegetable gums, the seaweed colloids and the hemicelluloses.

Industrially the sodium carboxymethylcellulose is more important than the analogous potassium salt whose properties are similar or the ammonium salt. The ammonia salt is water soluble but is unstable, losing ammonia on heating to 50 to 60°C.

The lead, silver, mercury and aluminum salts are colorless and insoluble, while the copper and nickel compounds are blue, the ferric salt red, and the metals which give colored ions give colorless salts. Only the alkali metal salts are soluble; the heavy metal salts are insoluble and only dispersible with difficulty.

Sodium carboxymethylcellulose is a hydrophilic colloid which shows "gum" characteristics of marked thickening, stabilizing, and film forming. It has been suggested for the usual water-dispersible gum applications as a protective colloid in emulsions, adhesives, agglutinants, finishing and sizing agents in textiles, paper coating, as well as others.

Feeding experiments have indicated on work with animals that the compound is physiologically harmless when ingested.

The details of the manufacture of carboxymethylcellulose and its salts are given by Jansen,[2] Chowdhury[3] and Höppler.[4]

This product is in three viscosity types:

Low viscosity	25-50 cps. in 2% solution
Medium viscosity	400-600 cps. in 2% solution
High viscosity	Approximately 1500 cps. in 1% solution

[2] Jansen (assignor to Deutsche Celluloid Fabrik Eilenburg), German Patent 332,203 (1918).
[3] J. K. Chowdhury, *Biochem. Z.*, **148**, 76-97 (1924).
[4] F. Höppler, *Chem.-Ztg.*, **66**, 132-5 (April, 1942).

The viscosity changes markedly with changes in concentration as shown for the low viscosity material in Table 27.

Table 27. Viscosity-Concentration Relation for Carboxymethylcellulose

Percent Concentration	Viscosity in Centipoises
0.5	27.7
1.0	68.8
2.0	1160
2.5	2840
3.0	5330
3.5	11580
4.0	34400
4.5	86300
5.0	115000

Although the solutions are quite stable to heat, there is some loss in viscosity on long exposure to elevated temperatures such as 70°C.

The effect of addition of salt solutions to solution of sodium carboxymethylcellulose is as follows: No effect is evident with magnesium sulfate, nitrate or chloride, calcium nitrate, chloride or acetate or manganous sulfate. Barium nitrate produces a thixotropic gel. Precipitates are obtained with ferric chloride, ferrous sulfate, stannous chloride, aluminum sulfate and basic lead acetate. Films cast from solutions to which have been added salts that cause no precipitation, redissolve readily in water. Films cast from sodium carboxymethylcellulose solution and painted with solutions of the other salts noted above, are insoluble in water, but except for that painted with lead acetate, they all dissolve in 5 per cent sodium hydroxide.

Equal volumes of a 2 per cent solution of this material and solutions of various acids were mixed and while no precipitate remained, the films cast from the resulting solutions were insoluble in water except the one cast from the acetic acid mixture.

The general properties of sodium carboxymethylcellulose are given in Table 28.

Sodium carboxymethylcellulose is compatible in varying proportions with many water soluble plasticizers, natural gums and other film formers. The results of compatibility tests in solution and in films are shown in Table 29.

Sodium carboxymethylcellulose is unaffected by the common organic solvents and oils. To inhibit mold growth it is sometimes necessary to add preservatives such as sodium benzoate, phenol, or chlorinated substituted phenols.

Sodium carboxymethylcellulose is suggested for use where gums gen-

Table 28. Miscellaneous Properties of Carboxymethylcellulose

Bulking density, gal./lb.	0.0688*
Refractive index (film)	1.525
Electrical charge (on film)	negative (very small)
Equilibrium moisture content on flake (after 48 hours), 77°F., 50% R.H.	12.2%
Charring	
Browning range	190°-205°C.
Charring range	235°-248°C.
Specific gravity of film	1.6
Specific gravity of solution	1.0088*

* Determined from 2% solution.

Table 29. Compatibility of Sodium Carboxymethylcellulose with Various Materials

	Ratio, Sodium Carboxymethylcellulose In Solution to Plasticizer In Film					
	3:1	1:1	1:3	3:1	1:1	1:3
Glycol	C	C	C	C	C	C
Glycerin, c.p.	C	C	C	C	C	C
Sorbitol	C	C	C	C	C	C
Invert sugar	C	C	C	C	C	C
Sodium silicate	C	C	C	SI	SI	SI
Starch (Baker's Soluble)	C	C	C	C	C	C
Casein	C	C	C	SI	SI	SI
Gum arabic	C	C	C	C	C	C
Tragacanth	C	C	C	C*	C*	C*
Sodium alginate	C	C	C	C*	C*	C*
Gelatin, Merck	C	C	C	C	C	C
Irish moss	C	C	C	C*	C*	C*
Cellosize WS	C	C	C	C	C	C
Pectin	C	C	C	C	C	C
Methyl Cellulose, 4000 cps.	C	C	C	SI	SI	SI
Polyvinyl alcohol (Grade RH-393)	C	C	C	SI	SI	SI
Polyvinyl alcohol (Grade RH-391-N)	C	C	C	SI	SI	SI
Animal glue	C	C	C	C	C	C
Tri-ethyl phosphate	C	C	C	SI	SI	SI
Glycolated melamine—formaldehyde resin	C	C	C	SI	SI	SI
Glycolated urea—formaldehyde resin	C	C	C	SI	SI	SI
Dimethoxydimethylurea	C	C	C	C	C	C

* Material tested forms cloudy film alone; compatibility was based on this cloudy film. C—Compatible SI—Slightly Incompatible

erally find application such, for example, as in a thickening agent in textile printing pastes, as an emulsifying agent in emulsion paints and lacquers, as a film former in paper sizing and coating particularly for greaseproof coatings, also in boiler compounds, latex, drilling muds, ceramics, can sealing compounds, leather finishing and insecticides.

"Cellosize" is an aqueous solution containing 10 per cent of hydroxyethyl cellulose. Viscosity of this solution is about equivalent to a winter grade of lubricating oil, but decreases on warming. It does not gel at higher temperatures as do methyl cellulose solutions. On drying, it produces an almost colorless, nearly transparent film of greater clarity and higher tensile strength than is obtained from commercial methyl cellulose solutions. The viscosity decreases on warming and, unlike the alkyl celluloses, it will not gel at higher temperatures. In contrast with polyvinyl alcohol, this hydroxyethyl cellulose film is completely soluble after drying, in either cold or hot water. Also, its light and heat stabilities are superior to those of polyvinyl alcohol. The characteristics are given in Table 30.

Table 30. Properties of "Cellosize"

Specific Gravity at 20/20°C.	>1.035
Concentration, %	>10
pH	6.0 to 7.0
Water Miscibility	Complete
Ash Content after drying, %	0.50 to 1.50
Viscosity (Hoeppler) at 20°C. after dilution with equal weight of water, centipoises	75 to 100
Flash Point	None
Dried film burns less readily than paper	
Average Weight per gal. at 20°C., lb.	8.6

"Cellosize" has been suggested for sizing applications in which starches, gums, gelatins, soluble resins, and other thickening agents are commonly used in textile finishing, paper sizing, and in shoe and leather dressings.

It can be applied to dyed and printed materials. In contrast to materials as British gums and other starches, this hydroxyethyl cellulose, when used as a thickening agent in textile-printing pastes, tends to increase the solubility of the dyestuff in the printing vehicle. Unlike starch and gelatin sizes it will not mold.

The solution is compatible with solutions of other water-soluble film-forming materials such as gum arabic, gelatin, and starch, making it possible to vary the flexibility and in other respects modify the characteristics of the hydroxyethyl cellulose film to a high degree. Films of good strength and flexibility are obtained by using gum tragacanth in such proportions that it is present in the final film to the extent of 20 per cent by weight.

The hydroxyethyl cellulose resulting from the drying of the water-soluble solution can be made temporarily water insoluble by the addition of glyoxal. Thus, when 5 parts by weight of 30 per cent glyoxal is dissolved in 50 parts of the WS solution and the water is evaporated with

subsequent drying at 105°C., a clear, glassy product of good tensile strength results. It is not affected by water except after soaking and it is insoluble in oils, greases, and organic solvents.

"Cellosize" hydroxyethyl cellulose is a good protective colloid for the aqueous dispersion of oils, fats, waxes, and pigments. It has been applied experimentally in the field of emulsion polymerization in the manufacture of synthetic resins and elastomers. With varnish bases it forms a water-in-oil type of emulsion that spreads evenly and dries to a smooth film. It also shows promise in water paints since it can bind large amounts of pigments. These finishes dry "flat" and do not rub off except when wet.

Chapter 9

The Modified Starches

Dextrin and British Gum

The dextrins and British gums are starch modifications as a result of the action of heat or of heat and chemical agents by dry processes, or the conversion products of starches manufactured by suspending starches in water or cooking them to jellies and acting on these with chemical agents either in the cold or at higher temperatures. The dry methods involving thermal processing are the more important.

Bouillon Lagrange made dextrin by roasting starch in 1804. He was attempting to find a substitute for gum arabic or gum tragacanth which were then largely used in industry. He published a description of his method and product in 1811. Biot and Peroz[1] in 1833 studied the gum formed by the action of dilute acid on starch. Inasmuch as its optical rotation was to the right, he named the product dextrin.

British gum reputedly originated as a result of a fire in a starch storage building at a textile plant near Dublin, Ireland, in September 1821. Part of the factory was destroyed by fire and the starch in storage had been exposed to the heat and roasted to a brownish yellow color. When this material was mixed in cold water it no longer had the characteristics of a starch but dissolved to a viscous gummy liquid. The results were duplicated by heating starch in a cooking pot over fire and the manufactured material was henceforth known as British gum.

The American industry appears to have originated with the granting of a patent to V. G. Bloede in 1867.[2] Dextrin was made by dampening starch with a dilute mixture of nitric and hydrochloric acids. The mixture was spread upon sheet iron pans and exposed to the heat of a baker's oven until thoroughly dried and slightly yellowed. Bloede called the product gum regialine.

Up to 1870 the gums from the acacia tree, particularly the Sudan and gum arabics, were almost exclusively used for the gumming of papers, envelopes, and stamps. At the time of the Mahdist rebellion in the Sudan and the Sudanese campaign between 1884 and 1898, the supply of gum

[1] *Ann. chim. phys.*, **52**, 72-90 (1833).
[2] U. S. Patent 61,991.

arabic was short and unstable. Prices rose to such an extent that substitutes were imperative. Dextrin from Germany relieved the situation.

Dextrin is a difficult substance to define chemically, inasmuch as it exists in so many varieties whose character and mechanical properties depend upon the details of manufacture, time of heating, temperature, the use or non-use of converting agents, the character of the converting agent, as well as the raw material or mixtures of different starches as such raw material. The colors of dextrin may be from almost a pure white to a dark brown. Some grades are highly adhesive and dry quickly; others are different in viscosity, show a lower degree of adhesion and slower drying. Some are almost entirely soluble in cold water and others only partly so. Dextrin exists in many different modifications whose colloidal aspects are of importance. Its solution in water is colloidal and it diffuses through membranes. When heated above 225°C. it melts and decomposes. It is insoluble in absolute alcohol. When heated with dilute acids it is converted into dextrose. Concentrated acids decompose the material and carbonize it. On oxidation with nitric acid, oxalic acid is formed.

As a result of the inability to define dextrin, Bloede[8] suggests the specification of the Bureau of Printing and Engraving of the Federal Government of the United States as a description of dextrin.

"Specifications for Cassava Dextrin for the Bureau of Engraving and Printing, Treasury Department, Washington 25, D. C., December 21, 1944.

1. Intent: This specification contemplates the purchase of Cassava dextrin which shall be suitable for use as an adhesive for gumming stamps printed in the Bureau of Engraving and Printing.

2. Origin: The dextrin to be delivered under any contract resulting from this invitation shall have been converted in the United States from starch derived from the Cassava root.

3. Physical properties: The dextrin shall be of high quality and shall be in powdered form. It shall be preeminently adapted for use in gumming postage and internal revenue stamps. It shall be free from grit or other foreign matter and shall not be inferior to the bureau standard sample. After being applied to and dried on stamp sheets, it must be light in color, flexible, transparent, and of superior adhesive quality. The dextrin must be substantially neutral or have only a slightly acid reaction. It must have no objectionable taste or odor, and be not inferior to dextrin having the following analysis:

4. Analysis:

[8] Victor G. Bloede, "A Comprehensive Survey of Starch Chemistry," edited by Walton, Vol. I, Reinhold Publishing Corporation, New York, (1928).

Dextrin by polarization	88.6 per cent
Reducing substance, as dextrose	2.4 per cent
Volatile at 105°C.	1.8 per cent
Ash	.12 per cent
Material insoluble in cold water	.30 per cent
Polariscope reading 10 grams of dextrin in 100 cc. of solution	96.0 Ventzke scale
Refractive index at 25°C., 125 grams of dextrin plus 250 grams of water	1.3880
Viscosity, Engler, 20°C., solution made by dissolving 125 grams of the sample dextrin (including moisture) in 250 grams of water, after standing for 3, 24, and 48 hours respectively (the water time of the Engler viscosimeter now in use by the bureau is 51.4 seconds at 20°C.	200-250 seconds

5. Storage characteristics: When formulated according to the bureau standard formula and allowed to stand for five days in an open container, the dextrin must not thicken more than does the standard sample. The increase in viscosity on standing shall be so small that a cold solution will flow through the bureau gum lines, after standing, without overloading the gum-circulating pumps.

6. Working characteristics: Samples of dextrin will be formulated according to the bureau standard formula and given a practical trial during which they will be rated on color, flexibility, and adhesive quality.

7. Formula: The dextrin now used for gumming postage stamps is formulated as follows: 750 pounds of dextrin is incorporated in 412 pounds of boiling water."

Bloede[4] states that one part of this dextrin dissolved in one part of hot water produces a clear thin liquid of light amber color and of high adhesive properties, the solution remaining of uniform consistency and clearness on cooling.

In general the raw materials for dextrins are the starches such as corn, sago, tapioca, and potato, with some smaller uses of starches from other sources. The dextrin products vary considerably in their characteristics as a function of the raw material as well as the manufacturing operation. While potato starch is thought of as the easiest one to convert, disagreeable odors are produced by thermal processing. Tapioca is free from this objection, in that the dextrin made from this raw material is in most cases odorless and tasteless while giving good adhesive strength, solubility, color, viscosity, and clarity. When sago starch has been refined by washing or chemical treatment, satisfactory dextrins may be produced from it. It is claimed that the dextrins from cornstarch are not quite as good for some specialized purposes as that produced from tapioca or purified sago, but for most applications cornstarch dextrins are competitive with those

[4] *Loc. cit.*

from other sources in solubility, clarity, whiteness, adhesiveness, and viscosity.

There seems to be some question as to whether pre-drying of the starch in advance of conversion into dextrin is necessary or desirable. Bloede[5] proposed pre-drying and heating various starches for periods of time beyond the temperature necessary for the removal of natural moisture, claiming that special qualities were imparted to the dextrin upon hydrolyzation.

The manufacturing method is fairly simple and consists in lightly wetting or dampening the starch with hydrolyzing or catalytic agents. Typical ones are the mineral acids hydrochloric, nitric, sulfuric, or mixtures of these, the organic acids such as oxalic and formic, or the halogen acids including hydrobromic. Agents which are volatilized at the thermal processing temperatures are preferred, inasmuch as in their vapor or gaseous form they more completely penetrate the starch masses and make direct contact with the individual grains. It appears, however, that the processes of dextrinizing starch through the medium of acid vapors have had little success. Other chemical materials, such as acid salts or alkaline earth salts, which hydrolyze at the thermal processing temperatures, examples of which are magnesium and aluminum chloride, are quite effective. The chemical agents are commonly dissolved or diluted with water and the solution mechanically mixed, in rotating agitators or by means of stirrers, with the starch. Diffusion of the hydrolyzing agent throughout the mass occurs during holding or storage periods. The hydrolyzing agent is employed in amounts of the order of 0.03 to 0.5 per cent, these amounts being determined by practical experiments and varying with different starches or different shipments of presumably the same starch.

Many different forms of apparatus for dextrinizing have been suggested or have come into use. In the early forms the apparatus consisted of a heated room or a drying chamber in which the starch in the form of premolded shapes or powders spread on trays was subjected to temperatures of the order of 200 to 300°F. for several hours.

Ullmann[6] describes a number of German furnaces consisting of shallow pans with rotating rakes mounted over heating chambers, as well as cylindrical drums with spiral agitators, the drums being set horizontally with external heating. In some more elaborate mechanisms these are in the form of cylindrical driers mounted one above the other and discharging one into the other. It is necessary that the heating be very even and uniform and that the starch be kept in constant motion and completely

[5] U. S. Patent 1,324,332 (1919).
[6] Fritz Ullmann, "Enzyklopädie der technischen Chemie," Vol. 3, Urban and Schwarzenberg, Berlin, 1916.

agitated. Considerable care must be taken in the design to prevent any corners or pockets in which the starch may lodge and be unevenly processed.

In general, the temperatures employed for dextrins and British gums are between 230 and 400°F. For the grades of dextrin made at 250 to 300°F., steam heating is often employed although this method of addition of thermal energy is not adapted to British gum which is normally produced at temperatures of 400° or over. In the processes reaching temperatures of 350 to 400° or higher, heating is by direct or indirect mechanisms employing gas, oil, or other fuels. Some use has been made of preheated oil in circulating systems in jacketed apparatus and to a limited extent electrical heating has been used.

When the raw material has reached the proper stage of conversion for the particular dextrin or British gum being manufactured, it must be removed and rapidly cooled, usually with high velocity air.

It does not seem possible, in view of the variations in the starches, their different characters, variation in shipments of the same starch, the engineering aspects of the thermal processing equipment, and the wide number of dextrins of different characteristics needed for the trade, to set down operating procedures of a concise nature. Processing times, for example, may be from 1 to 10 hours.

The trade differentiates between dextrins and British gum in that the latter gives higher viscosity dispersions or very thick masses or even nonflowing pastes. Part of these characteristics are owing to the presence of starch only partly converted. British gum may be made by simple thermal processing of the starch without the use of a hydrolyzing agent or with amounts much smaller than that employed for the preparation of dextrin. The British gums are usually somewhat darker, being browner in color and often having a distinct burnt or empyreumatic odor. Dextrins are often made from single starches, while British gums are commonly produced from mixtures of starches either in their raw material state or after conversion into British gum.

Alkaline conversion products of starches have been known as vegetable glues and are competitors of the animal glues for application as adhesives and mucilages. One of the most common processes employed consists of suspending tapioca or cassava in water, the starch-water ratio being 1:2.5 to 1:4, and adding caustic soda in concentrations of the order of 3 to 5 per cent. This composition is heated while being continuously agitated to the bursting point of the starch granule. This bursting point is of the order of 100 to 120°F. A stringy glue-like mass which shows high adhesive characteristics results.

One of the first vegetable glues was produced in France in 1874 by

Table 31. Analysis of Continental Dextrins and British Gums

Commercial Name	Per Cent Moisture	Cold Water Solubles				Insolubles		Acidity, cc. of Normal Alkali per 100 g. Dextrin	Color	Marking	Color with Iodine
		Maltose	Dextrin	Other Organic Compounds	Mineral Matter	Hulls and Residues	Silica and Mechanical Impurities				
Artificial gum	10.14	5.37	69.85	11.99	0.40	2.06	0.19	3.5	Light sulfur yellow	Acid dextrin	Red brown
Yellow gommeline	9.01	8.85	66.79	12.34	0.56	2.13	0.32	4.6	Dark yellow	Acid dextrin	Red brown
Dextrin	8.42	10.45	63.76	12.97	0.46	3.65	0.29	4.4	Light sulfur yellow	Acid dextrin	Red brown
German dextrin	7.55	14.11	62.37	13.13	0.41	2.20	0.23	4.7	Light sulfur yellow	Acid dextrin	Red brown
Leiogomme	12.08	4.20	56.46	7.80	0.56	18.49	0.41	3.1	Dark brown	Roasted dextrin	Red brown
Leiogomme	12.01	1.75	53.52	10.70	0.42	21.39	0.21	2.7	Gray yellow	Roasted dextrin	Red violet
French thick gum	13.36	1.59	48.19	8.80	0.38	27.58	0.10	2.5	Gray yellow, somewhat lighter	Roasted dextrin	Red violet
White gommeline	13.30	4.00	25.37	3.02	0.20	53.84	0.27	2.8	Pure white	Acid dextrin	Blue violet

Gerard[7] and given the trade name Apparatine. Perkins[8] patented related processes in the United States in 1912.

Despite the apparent lack of concise details in the preparation of dextrins and British gums, these materials may be considered as manufactured products which can be reproduced in large quantities to meet commercial specifications. They are therefore "synthetic" competitors of the natural gums which for many industrial applications they have completely replaced. A typical example is on envelopes and stamps of the mail and revenue type which, in their early history, employed gum arabic but which application has been completely replaced by specific varieties of dextrins known as envelope gums. In their manufacture these materials employ smaller percentages than usual of hydrolyzing agents, higher temperatures, and shorter times of thermal processing than have been described for the other dextrins.

Ullmann[9] gives the analysis of a number of Continental dextrins in Table 31.

[7] French Patent 102,200 (1874).

[8] Perkins Glue Co., U. S. Patents 1,020,655, 1,020,656 (1912), 1,078,691, 1,078,692 (1913), 1,200,488 (1916), 1,251,275 (1917), 1,267,699 (1918), 1,299,705, 1,299,809, 1,311,965 (1919), 1,378,078, 1,378,106, 1,378,128 (1921).

[9] Fritz Ullmann, "Enzyklopädie der technischen Chemie," Vol. 3, Urban and Schwarzenberg, Berlin, 1916.

Chapter 10

The Water-Dispersible Proteins

The water dispersible proteins of major commercial importance are: gelatin, hide, bone, fish, and other glues, casein, soya bean protein, and the various albumins.

These materials might be considered as "gums" in the sense of adhesives or glues. In this respect it is to be noted that the gums discussed in this volume swell in cold water, they gel on cooling when they are in the form of a lyophilic sol, they melt on warming, and gel again on cooling. On drying, the strength of the jelly increases. Of the protein materials, only gelatin and glue are in this class so that a brief consideration of gelatin as a gum is desirable for a well rounded discussion. It is to be noted that the literature on gelatin is extensive.[1]

The albumins, however, usually require heating to temperatures of the neighborhood of 100°C. to bring about gelation. They do not have the same characteristics as the "water-soluble" gums such as gum arabic and therefore are not considered in this volume. The chemistry of the albumins has been extensively treated in studies of the proteins.

Casein gels without temperature change as a result of chemical reaction taking place slowly in a solution of a sol. Casein is water dispersible through the media of alkalies so that alkali or alkaline earth caseinates are formed. These are stable only in gel form and slowly change to jellies. These characteristics markedly differ from the gums, and casein is therefore outside of the scope of this volume. The chemistry and applications of casein are the subject of a voluminous literature.[2]

The glues or adhesives that gel through evaporation of water as a solvent include the British gums, dextrins, vegetable mucilages, hemicellulose seed extracts and the true gums such as arabic and the like. The chemistry of these materials has not been the subject of the intensified study as has been accorded the proteins. Much of the coordinating colloidal chemical theories have been developed as a result of study of the

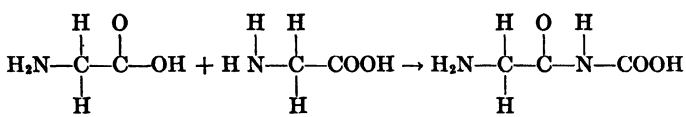
[1] Bogue, "The Chemistry and Technology of Gelatin and Glue," McGraw-Hill Book Company, Inc., New York, 1922; J. Alexander, "Glue and Gelatin," Am. Chem. Soc. Monograph, Chemical Catalog Co., New York, 1923; Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Company, Inc., New York, 1922.

[2] E. Sutermeister and F. L. Browne, "Casein and its Industrial Applications," Reinhold Publishing Corporation, New York, 1939.

proteins. This work has not been as intensively applied as it can and will be to the gums and thus aid in understanding them and improving their usefulness.

Because of the great importance of the proteins to the biochemist, far more work has been done on them than on water-dispersible colloids such as the gums. Only that part of these studies which reflects the commercial utilization will be summarized here.[3] A better understanding of the chemistry of the proteins will help in the understanding of the behavior of the non-protein sols and gels.

Proteins are complex organic compounds which on hydrolysis ultimately yield mainly α amino acids. Amino acids are the primary decomposition products of proteins, and the proteins themselves may be regarded as condensations of amino acids with the elimination of water. According to Fischer the amino group of one amino acid is condensed with the carboxyl group of its neighbor to form a peptide linkage —NH—CO— as in the example of two glycines condensed below:



The more complex proteins apparently consist of ring structures, but no attempt will be made here to discuss this phase of the subject.[4] Less complex proteins such as the hydrolytic product of collagen, which is gelatin, are in themselves quite complex and contain ring as well as straight chain structures.

The proteins such as gelatin and casein are not single entities, but rather mixtures with certain common properties which distinguish them from other proteins and non-proteins. These properties are somewhat affected by their history, such as their thermal treatment, pH, and methods of extraction. Sorensen has postulated that protein solutions consist of a complex of reactive ingredients that readily undergo association and dissociation.

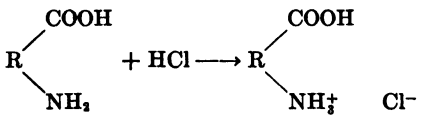
As the proteins are condensations of amino acids through polypeptide linkages, we would expect the proteins like the amino acids to be

[3] For more detailed discussion of the chemistry of the proteins, the following are recommended: E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corporation, New York, 1943; D. J. Lloyd and A. Shore. "Chemistry of the Proteins," J. and A. Churchill, Ltd., London, 1938; W. Clayton, "Colloid Aspects of Food Chemistry and Technology," J. and A. Churchill, Ltd., London, 1932; A. W. Thomas, "Colloid Chemistry," McGraw-Hill Book Company, Inc., New York 1934.

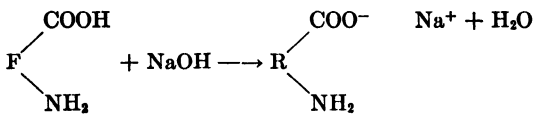
[4] For a good summary and bibliography see D. J. Lloyd and A. Shore, "Chemistry of the Proteins," Chapter VIII, on "The Architecture of the Protein Molecule," J. and A. Churchill, Ltd., London, 1938.

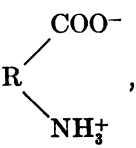
amphoteric, that is, capable of combining with acids or with bases except at the isoelectric point where they combine with neither acid nor base. The isoelectric point will be discussed in a later section of this chapter.

The mechanism whereby proteins neutralize acids and bases is explained by the older theory as follows. The amino acids or proteins exist in aqueous solution in a completely or nearly completely un-ionized form, acids reacting with the $—NH_2$ group to form $—NH_3^+$ ion and bases with the —COOH group to form $—COO^-$ ion:

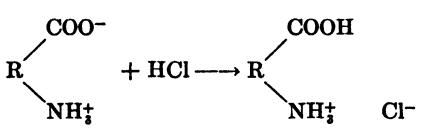


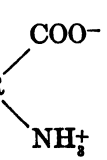
and



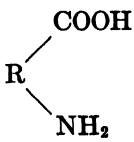
A more recent hypothesis[5] postulates that the amino acids and proteins exist in aqueous solution in a completely ionized form,  , referred to as Zwitterions, amphoteric ions, or dipolar ions.

According to the older theory an increase in alkalinity permits ionization of the weak COOH group, and the weak basic $—NH_2$ group is dissociated only in acid solutions. According to the Zwitterion theory, the effect of acid addition is to repress ionization of the COOH group leaving the $—NH_3^+$ radical free electrostatically balanced by the anion of the added acid:



The Zwitterion  may also exist as an uncharged molecule

[5] Adams, *J. Am. Chem. Soc.*, **38**, 1503 (1916); Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923).



and either may go over to the other form through interchange of a hydrogen ion between carboxyl and amino group. The position of equilibrium between the Zwitterion and the uncharged molecule depends upon the acidic and basic properties of the group involved. The aliphatic amino acids in water exist almost entirely in the Zwitterion form, the amino benzoic acids as mixtures of both forms, and the aminophenols almost entirely in the uncharged form.

An essential difference between the two theories consists in the strengths to be ascribed to the acidic and basic groups, for example, the acidic and basic groups of glycine by the older theory are many times weaker than acetic acid and ammonia, while by the new theory, they are each slightly stronger. Neither theory, however, satisfactorily "explains" all the ionization phenomena, and it is therefore necessary to consider the mechanism from both viewpoints. In both theories the protein is the cation in the protein chloride and the anion in sodium proteinate, e.g. sodium gelatinate.

The acidity of a group depends primarily on the nature of the group itself, and secondly on the nature of neighboring groups in the molecule. In simple amino acids, the acidity is a function of the acid groups such as carboxyl, phenolic or sulfhydryl, and the basic groups such as ammonium ion and its derivatives. Substitute groups such as methyl and phenyl, and their position in the molecule also profoundly affect the degree of acidity. In the protein, the sum total of acid and base combining capacities and the properties of the proteins such as swelling, viscosity, osmotic pressure and isoelectric point, become a function of all the involved behavior of the constituent amino acids and the type and degree of their linkages with one another.

Isoelectric Point. Since proteins and amino acids are amphoteric, there must be a hydrogen ion activity (or pH)[6] at which its positive and negative charges are equal to each other and this region of electrical neutrality is called the isoelectric point. At the isoelectric point, there is no migration of protein in an electrical field, and many properties are affected. For example, solubility, stability, conductivity, swelling, viscosity, and osmotic pressure are at a minimum at or near the isoelectric point. Addition of acid to a protein at the isoelectric point yields a pro-

[6] The convenient method of expressing hydrogen ion concentration according to Sorensen's suggestion in 1909 is now quite general, $pH = \log_{10} \frac{1}{H^+} = -\log_{10} H^+$.

tein with a positive charge, *e.g.*, gelatin chloride which ionizes to gelatin$^+$ ion and Cl^- ion. Addition of alkali to a protein at its isoelectric point yields sodium proteinate which ionizes to protein ion and Na^+ ion. Titrations of proteins have been carried out with acids and bases and the stoichiometric nature of the titrations has been demonstrated.[7]

Treatment of a protein which alters its acidic or basic nature changes its isoelectric point. Different hydrolytic treatments of collagen yield gelatins of different isoelectric points. Gelatin from an acid swollen ossein gave an isoelectric point of 5.5 to 6.5, and from an alkali swollen ossein 4.9 to 5.1.[8] Since hydrolysis sets free groups of amino acids or amino acids themselves and since these each have different isoelectric points, it is seen why different hydrolytic treatments give varied isoelectric points. Formaldehyde treatment of a gelatin shifted its isoelectric point from 4.75 to 4.3.[9] Nitrous acid deamination treatment shifts the isoelectric point to a lower pH.[10] Addition of neutral salts may also shift the isoelectric point, sodium chloride may lower it for casein from 4.6 to almost 4.0. A list of isoelectric points of some proteins is shown in Table 32.

Table 32. Isoelectric Points of Proteins[1]

Proteins	Isoelectric Point
Albumin (cow's milk)	4.6
Albumin (hen's eggs)	4.6-5.0
Albumins (seeds)	4.2-5.1
Albumins (serum)	4.7-5.2
Casein (cow's milk)	4.6-4.9
Collagen (hide powder)	5.0
Gelatin	4.4-5.6
Soybean protein	4.6

[1] A. W. Thomas, *J. Am. Leather Chem. Assoc.*, 29, 3 (1934); and others.

Solubility. Measurement of solubility of proteins is not as simple as in the case of crystalloids. It is often hard to distinguish at what point the gel passes into solution or, approaching the solubility from the other side by cooling, at what point the solution passes to a gel. When water or a solution is added to a dry protein, it first swells and if soluble, later passes into solution. Solubility is profoundly affected by the temperature, pH, length of time allowed for solution, age of solution, previous history of the protein, amount and kind of salts present, and kind of acid or alkali

[7] J. Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Company, Inc., New York 1922; Cohn, *Physiol. Rev.*, 5, 349 (1925).
[8] E. C. E. Hunter and A. J. Turner, *Trans. Faraday Soc.*, 36, 835 (1940).
[9] Gerngross and Bach, *Biochem. Z.*, 47, 260 (1914).
[10] Hitchcock, *J. Gen. Physiol.*, 6, 95 (1923); Z. C. Loebel, *J. Phys. Chem.*, 32, 763 (1928).

present. At or near the isoelectric point, solubility is at a minimum. Acid added to the protein at the isoelectric point lowers the pH and the solubility rises to a maximum and then falls, probably due to a dehydrating action on the protein by the larger amounts of acids. The kind of acid affects the extent of the solubility. For example, casein is more soluble in phosphoric acid than in hydrochloric acid, less soluble in nitric monochloracetic, tartaric, and lactic acids, and is only slightly soluble in sulfuric, acetic, oxalic, and trichloracetic acids.

Solubility in aqueous alkalies, unlike solubility in aqueous acids, does not attain a maximum and then fall off again as the pH is increased. Moreover in alkaline solutions the solubility is increased by the addition of alkali salts in moderate concentration. The solubility of proteins is about equal in solutions of sodium, potassium and ammonium hydroxides and decreases in $Sr(OH)_2 > Ca(OH)_2 > Ba(OH)_2$.

In acid solutions, solution is preceded by swelling with absorption of the acid solution and formation of cationic protein. In alkali solution the alkali proteinate lowers the interfacial tension so that small particles of the dissolving protein are torn off permitting more rapid penetration of the alkali into the protein and repetition of the tearing apart. Velocity of solution is more rapid, and swelling plays a less important role than in acid.

Sorensen[11] has suggested that the proteins should be regarded as mixtures of components held together by secondary valences and capable of reversible association and dissociation. The more soluble proteins are those that are more highly dissociated electrolytically in solution and are hydrated (bind water) in solution. Hydration occurs at the free amino, carboxyl, and phenolic hydroxyl groups, while at the peptide linkages little hydration can occur. At the isoelectric point, amino and carboxyl groups neutralize each other and any excess of amino or carboxyl groups is almost entirely un-ionized as in the case of the higher fatty acids. The result is that association dominates over hydration and the solubility is low. Addition of reagents which increase the number of highly ionized groups, such as hydrochloric acid and sodium hydroxide, cause increased hydration and solution.

Colloidal Behavior. Solutions of proteins behave in many respects unlike the solutions of ordinary crystalloids. They behave more like small particles or micelles dispersed in the liquid and the term "sol" is used in place of solution. The precipitates or jellies obtained are called "gels" and the process of forming sols is called "peptization." Micelles are regarded as aggregates of molecules or ions or macromolecules, very large molecules. Largely as a consequence of the size of the dispersed

[11] Sorensen, *Kolloid-Z.*, 53, 102, 170 (1930).

particles, colloids exhibit certain characteristics such as scattering of light ultramicroscopic visibility, separation on ultracentrifugal sedimentation, slower diffusion than crystalloidal ions, and impermeability to membranes of suitable porosity (e.g. collodion). The proteins also can form highly viscous sols and stiff gels. They also have emulsifying properties and form films around other particles ("protective" action). At the same time that they exhibit these non-crystalline characteristics they also combine with acids and bases as would be expected from the basic and acidic groups in their chemical structure.

Effect of pH. The effect of pH upon solubility has already been discussed. Osmotic pressure, swelling, and viscosity are affected by acids and alkalies (and salts) in a very similar way suggesting that all are due to the same cause.[12] Osmotic pressure determinations were made by placing inside collodion bags, 1 gram of protein in 100 cc. of solution containing varied amounts of acid (or alkali). The collodion bags were suspended in solutions of the same acid (or alkali), the pH outside the bag being the same as that inside. Osmotic pressure after 18 hrs. was measured and found to give values as shown in Fig. 44. The osmotic pressure is at a minimum at the isoelectric point rising to a maximum at a higher pH. Loeb postulated that the nature of acid or alkali does not influence the osmotic pressure of the protein solutions, but the valency does. Thus the monobasic acids or those that ionize like a monobasic acid (e.g., phosphoric acid) influence the osmotic pressure more than does a strong dibasic acid like sulfuric acid. It is, however, now generally believed that the nature of the acid is also a factor. Loeb argued that when the acid (or alkali) is added to the protein, an ionizable protein salt results, the amount being dependent upon the amount of acid (or alkali) added. This ionization is the cause for the osmotic pressure owing to the inability of the protein ions to diffuse through the collodion, though the crystalloidal ions of the acid are diffusible. There arises an unequal distribution of the diffusible ions on either side of the membrane (bag) and herein lies the behavior of proteins. The theory of ionic distribution of diffusible and non-diffusible ions originated with Donnan.[13]

Donnan's theory of membrane equilibria and the Proctor-Wilson theory which applied Donnan's theory to swelling phenomena will be treated briefly. Excellent accounts of these are given at length by Lloyd and Shore,[14] and Cohn and Edsall[15] and most other good books on col-

[12] J. Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Company, Inc., New York 1922.

[13] F. G. Donnan, *Z. Elektrochem.*, 17, 572 (1911); *Chem. Rev.*, 1, 73 (1924).

[14] D. J. Lloyd and A. Shore, "Chemistry of the Proteins," J. and A. Churchill, Ltd., London, 1938.

[15] E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corporation, New York 1943.

loidal chemistry. According to Donnan's theory if a membrane separates two solutions at equilibrium, the concentrations of a pair of diffusible anions and cations are equal on the two sides of the membrane. When there are non-diffusible ions (such as protein$^+$) on one side of the membrane the distribution of diffusible ions on either side of the membrane

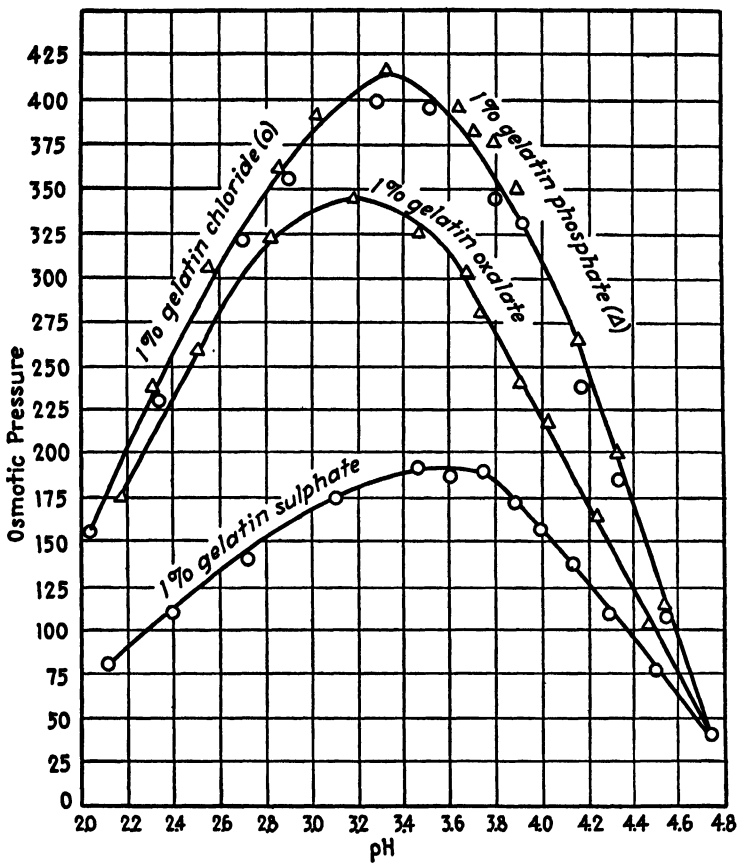


FIGURE 44. Influence of pH and valency of anion on osmotic pressure of solutions of different gelatin-acid salts.

still follows Donnan's equilibrium even though, for example, protein chloride is formed on one side of the membrane, say side "A." Let the other side be called "B." Assuming complete ionization of the protein chloride, in "A" there will be protein$^+$ ions, chloride$^-$ ions and hydrogen$^+$ ions while in "B" there will be chloride$^-$ and hydrogen$^+$ ions. While diffusion of hydrogen$^+$ and chloride$^-$ can occur, they can only occur in pairs, and since the protein ions can not diffuse, a corresponding number of chloride$^-$ ions

must remain in "A." There is accordingly in "A" a higher concentration of chloride$^-$ and a lower concentration of hydrogen$^+$ than in "B," though the product of their concentrations on each side is equal:

$$H^+_A \times Cl^-_A = H^+_B \times Cl^-_B$$

If x be the concentration of hydrogen$^+$ and chloride$^-$ in B and y and $(y+z)$ their respective concentrations in A, and a be the total concentration of the protein in A, then e the excess of diffusible ions in A will be:

$$e = 2y + z - 2x$$

and the osmotic pressure P will be:

$$P = RT(a + 2y + z - 2x)$$

Where the solution is dilute a is small and

$$P = RT(2y + z - 2x) = RTe$$

Since by the Donnan equilibrium

$$x^2 = y(y + z)$$

$$P = RT\frac{(x - y)^2}{y}$$

The calculated and observed values of osmotic pressure show good agreement and also account for the lower osmotic pressures at corresponding pH obtained with a strong dibasic acid, compared to those with a monobasic acid.

Proctor and Wilson used the Donnan theory to explain the swelling of proteins. If a gelatin gel is placed in a solution of hydrochloric acid, the gel itself acts as a membrane and the solution fills up the molecular interstices of the gel structure. Gelatin chloride forms and ionizes, but whereas the chloride ions exist in the interstitial solution, the corresponding gelatin cations are not in solution since they form part of the gel network. The chloride ions are balanced only by the positive charges on the network and as a result there is an unequal distribution of all ions between the interstitial solution and the external solution. The total concentration of chloride ions in the gel is greater than in the external solution. The anions of the gelatin chloride tend to diffuse into the external solution and so exert an attraction on the cations which form part of the gel structure. This causes an increase in volume—or swelling.

Effect of Salts. Salts affect the properties of proteins in several ways. They shift the isoelectric point and affect solubility, osmotic pressure, swelling, and viscosity. In dilute solutions at pH values away from the isoelectric zone, the effects of the salts of alkali and alkaline earth metals,

the electrostatic and valency effects predominate. In the more concentrated solutions lyotropic effects predominate.

Loeb has shown that at low concentrations (<0.1 M) salts always increase the swelling at the isoelectric point and depress the acid and alkaline swelling of gelatin gels. On the acid side of the isoelectric point the depression is a function of the anion, on the alkaline side a function of the valence of cation. Loeb explains this on the basis of a disturbance of the Donnan equilibrium and the Proctor-Wilson theory in which e is caused to decrease and the swollen jelly loses water and shrinks.

Salts influence surface tension of water, viscosity, temperature of maximum density, solubility of electrolytes and non-electrolytes, also stability and properties of aqueous colloidal solutions. The effect of salts depends on the nature of the anion and cation. Hofmeister[16] showed that salts could be arranged in order of their effective influence. The Hofmeister (or lyotrope) series Li>Na>K>Rb>Cs for the cations of the alkali metals and SO_4>Cl>Br>NO_3>I>CNS for the anions have been found to exist for a number of phenomena in crystalloidal and colloidal solutions and to be independent of changes due to specific activity of the hydrogen ion. The lyotrope series has also been shown to run parallel to the order of the hydration of the ions, the most highly hydrated (e.g., Li and SO_4) of the above series being at one end and the least hydrated (e.g. Cs and CNS) at the other. It is noteworthy that the salts with the greatest solubilizing action on proteins, e.g. LiCNS and LiI, have the most highly hydrated cation and the least hydrated anion. This same strong solvent action is paralleled with these salts on cellulose.[17]

With all lyophilic (water loving) colloids there is a competition between colloid and salt ion for the water molecules. In proteins with their Zwitterion constitution there will also be an attraction between the charged centers of the protein molecule and the salt ions.

Owing to the mutual attraction of water molecules for each other the non-attracting (non-polar) groups of the proteins tend to be squeezed out of an aqueous solution, a tendency increased by the presence of salts. In concentrated salt solutions there frequently occurs therefore a salting out of the proteins. Salting out is affected by pH. In strongly acid solutions the precipitation by salts shows the lyotropic series but in the reversed order, i.e. CNS is most efficient. Salts also shift the isoelectric point. In the isoelectric zone, additions of salts first increase, and with greater concentration then depress the osmotic pressure of gelatin. In the acid range dilute salt solutions depress the osmotic pressure, swelling and viscosity

[16] Hofmeister, *Arch. exp. Path. Pharmakol.*, **25**, 13 (1888); **28**, 210 (1891).

[17] D. J. Lloyd and A. Shore, "Chemistry of the Proteins," Chapter XII, on "The Specific Effects of Salts on Protein Solutions," J. and A. Churchill, Ltd., London, 1938.

of gelatin according to concentration and valency. In a more concentrated solution lyotropic effects become apparent even in acid solutions.

The swelling of gelatin in the absence of salts is a function of pH, with a minimum in the isoelectric zone and maxima at about pH 3 and 12. Additions of saturated solutions of alkali and alkaline earth compounds at the isoelectric point affect the swelling according to the Hofmeister series. At pH 3 and at pH 9 the effect of salts is repressed, their influence being dependent upon the Donnan effect. In concentrated solutions of strong alkalies, salts always increase the effects of the alkali. The concentration of salt is also a factor in deciding whether electrostatic or lyotropic influence is more conspicuous. In dilute solutions the former, in concentrated solutions the latter predominates, but both influences are always present.

Gelatin

Gelatin and glue, which is essentially an impure gelatin, are important proteins in commerce. Glue is used in far greater quantity than gelatin. United States annual consumption of glue is about 88,000,000 pounds, against somewhat over 30,000,000 pounds of gelatin. Much of their chemistry is alike, so that much of what is said here for gelatin is also applicable to glue. Glue and gelatin, however, are not competitive.

Gelatin is in competition with the hydrophilic gums, the plant exudations, the seaweed colloids, and the modified celluloses in many industrial applications. In photographic application gelatin stands alone. Gelatin has been more thoroughly studied than have the other hydrophilic materials and a knowledge of gelatin aids in the application of competitive materials particularly when divergent properties are considered.

Gelatin comes to market as sheets, flakes, and powder in various grades which fall into three broad groups, edible gelatin, photographic, and inedible (or technical) gelatin. The latter is often graded as sizing gelatin and pharmaceutical gelatin. The edible is by far the largest tonnage item. United States production figures for photographic gelatin are not available, but the United States Tariff Commission[18] gives production and import data for the others, and import data for the photographic group.

Edible gelatin is produced in various grades in the United States almost invariably blended from several batches to attain a uniformity, and is marketed chiefly in powdered and flake form. In foreign countries much is sold in sheet form. Edible gelatin is graded on the basis of "bloom" (a test of gel strength which will be described later in this chapter), color,

[18] U. S. Tariff Comm., Rept. No. 135, "Glues, Gelatins, and Related Products," 2nd Ser., p. 83 (1940).

odor, low sulfur dioxide content, low metallic content, and low bacterial count.

Photographic gelatin, also called emulsion gelatin, is second in tonnage consumption to the edible gelatin. Photographic gelatin requires exceptional control in its manufacture since small differences in content or behavior may render it unfit for the user. Each individual manufacturer of photographic film, plate, or papers requires for each of his different types of films, plates, and papers, a gelatin that behaves in what has been determined by trial and error as a satisfactory manner.

Inedible gelatin is similar in appearance and form to edible gelatin, but may contain impurities which the United States Food and Drug Administration would not permit in edible gelatin.

Methods of Manufacture.[19] Gelatin is obtained by the hydrolysis of collagen and ossein. Collagen is a scleroprotein contained in the skin, sinews, and tendons in animals like the calf, cattle, goat, sheep, pig, and horses. Ossein is the protein contained in bones. The principal raw materials, finished products, and byproducts are shown in Fig. 45.

Tanning-hide trimmings and other sources of collagen after a brief preliminary soaking or washing in water to soften them and remove dirt and salt are placed in successive baths of lime water of increasing strengths in order to swell the stock so it may be more readily dissolved in the boiling kettle, in order to loosen and dissolve out objectionable materials such as hair, blood, mucins, globulins and albumins, and in order to convert fatty impurities to insoluble lime soaps which rise to the surface as a scum, removable by washing through a screen. The lime treatment varies in time depending upon the character of the stock and the warmth of the season. The limed stock is removed from the lime pits to a washing machine where it is washed practically free of lime with water. The slight remaining alkalinity is neutralized with very weak acid, frequently with sulfurous acid which also serves as a bleaching and antiseptic agent. The stock is extracted several times with hot water. The first extract is with water at 60 to 70°C. and the successive extracts are at higher temperatures, the last sometimes at over 100°C. in an autoclave. In the first extract the most soluble material is removed with little hydrolysis of the extracted gelatin, and the first extract has better color, better gelling power, and higher viscosity than the subsequent extracts. The last extracts are frequently an inferior quality of glue. The extracts are filtered. For

[19] For a more complete description see Bogue, "The Chemistry and Technology of Gelatin and Glue," McGraw-Hill Book Company, Inc., New York, 1922; Alexander, "Glue and Gelatin," American Chemical Society Monograph No. 11, Chemical Catalog Company, New York, 1923, Chapter 43; J. Alexander, "Glue and Gelatin," in Rogers' "Industrial Chemistry," II, 6th Ed., D. Van Nostrand Co., Inc., New York, 1942.

further clarification egg or blood albumin may be added, the solution warmed and the clear liquor siphoned off from the coagulated impurities. In order to obtain a more uniform product, corresponding extracts of several batches are mixed. The solutions set to a firm jelly by cooling, and are converted to dry powder, flake, or sheets as desired.

When bones are the source of the gelatin, the process is essentially the

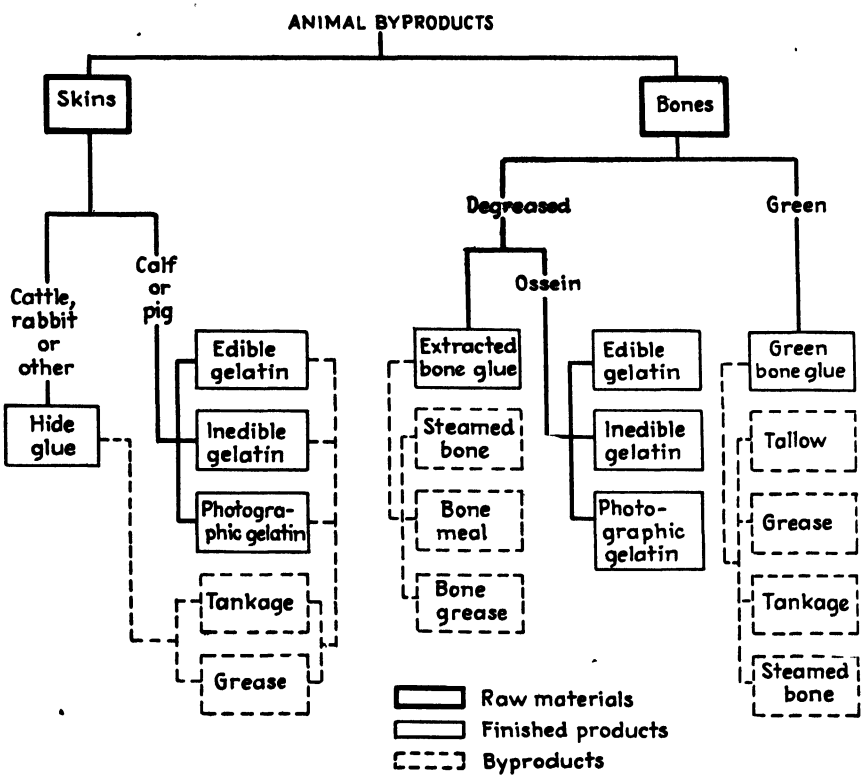


FIGURE 45. Animal glues and gelatins. Principal raw materials, finished products and byproducts.

same except that the bones are first degreased with organic solvents and the calcium phosphate and other mineral constituents dissolved out with cold dilute hydrochloric acid.

Many persons in the trade and literature refer to the first run (or extract) products as gelatins, those of the later runs as glues. Thus the properties of higher gel strength and viscosity together with lighter color are associated with gelatin, while low gel strength and viscosity together with darker color are associated with glue. On the other hand, some con-

sider the entire run of products as glues, and gelatin a clarified and bleached glue which may not possess higher gel strength and viscosity than a glue. A first-run gelatin has no significance since if it is made at high temperature and for a long period it may be a product inferior to a second run from another batch in which the extracts were at lower temperatures and for shorter periods.

An understanding of the variations of types and grades of gelatin is important in the selection of a gelatin for any specific purpose.

Specifications for Standard Gelatin.[20] An American Chemical Society Committee on Standard Gelatin reported that more than one standard for gelatin is necessary since there are different kinds of gelatin such as pigskin, calfskin, ossein, bone, etc., and inasmuch as the previous history of gelatin affects its character, and inasmuch as some gelatins are cooled on the acid side of the isoelectric point while others are cooled on the alkaline side. To simplify the situation, one standard gelatin was selected, from the scientific rather than commercial standpoint.

The tentative specifications for standard gelatin for physio-chemical purposes were adopted:

1. The gelatin should be calfskin gelatin made from green stock, limed for 3 months, scoured, washed, and extracted at 130°F. (54.4°C.), only the first run being used. The gelatin should be dried at not less than 5 per cent concentration which may require vacuum evaporation of the stock.
2. The gelatin should be de-ashed to an ash content of not greater than 0.05 per cent.
3. The gelatin should have a constant isoelectric point.
4. Under standardized conditions and at a definite given concentration it should have a definite viscosity.
5. Under standardized conditions and at a definite given concentration it should have a definite jelly strength.
6. The gelatin must be clear—that is, have a minimum turbidity in a 5 per cent jelly.
7. The gelatin must be free from color, i.e., have a minimum absorption of blue light at a definite thickness of a 5 per cent jelly.
8. The gelatin should have a minimum content of fat or grease (preferably less than 0.1 per cent).
9. The gelatin should contain not more than a minimum of 0.1 to 0.2 per cent of heat coagulable protein.
10. Inasmuch as isoelectric gelatin is being used, preservatives should be absent.

The committee believed that the specifications enumerated for stand-

[20] *Ind. Eng. Chem., Anal. Ed.*, 1, 56 (Jan. 15, 1929).

ard gelatin for physio-chemical purposes could apply to a standard gelatin for biochemical and bacteriological purposes with some additions.

As regards heavy metals, it shall not contain arsenic in excess of 0.5 p.p.m. as arsenic oxide. It shall not contain zinc in excess of 20 p.p.m. It shall not contain copper in excess of 10 p.p.m. It shall not contain other heavy metals in excess of 50 p.p.m. The methods of determining these metals shall be those prescribed by the Association of Official Agricultural Chemists.

Chemistry. Gelatin may be viewed as a protein derived from collagen by hydrolysis or as a condensation product of a number of amino acids. An ash-free isoelectric gelatin of highest purity showed[21] an ultimate composition of:

Carbon	50.5%
Hydrogen	6.8
Oxygen	25.2
Nitrogen	17.5

Small amounts of sulfur and phosphorus are also present.

An approximate makeup of hydrolytic products of gelatin is shown in Table 33.

The amino acids are condensed through peptide linkages to form groups of larger amino acids. Collagen in turn is a condensation product of gelatin. As the condensations continue, the molecular structure is not merely one of straight chain elongation, but takes cyclic forms as well so that for gelatin, absorption of an acid solution results first in swelling and finally may result in solution, whereas in the more condensed collagen with its fewer free amino and carboxyl groups, swelling occurs but not solution, unless hydrolysis to gelatin occurs. With drastic hydrolytic action on collagen, the hydrolysis may proceed through the gelatin stage producing smaller groupings of amino acids, and even ammonia. Hydrolysis of collagen with alkali may proceed to a stage where free ammonia is liberated and the resulting "gelatin" will have a lower than usual isoelectric point because there will be more free carboxyl groups.[22]

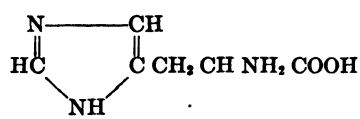
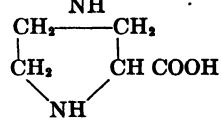
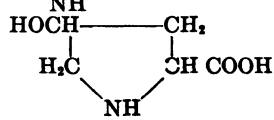
In the hydrolysis of collagen and ossein, linkages are broken which may open ring structures and may also split off groupings of amino acids or amino acids themselves, and the more severe the hydrolytic treatment, the greater the tendency toward breakdown to the amino acids and to ammonia. If the hydrolytic action is not severe the gelatin obtained behaves like a mixture of large molecules and the molecular weight is large.

[21] A. Allen, "Commercial Organic Analysis," 5th Ed., p. 131, P. Blakiston's Son & Co., Philadelphia, Pa., 1933.

[22] J. Beek, Jr., and A. M. Sookne, *J. Am. Leather Chem. Assoc.*, **34**, 641 (1939).

Ultracentrifuge studies[23] indicate molecule weights from 11,000 to 70,000. Published molecular weights vary widely but this is understandable since the amount of breakdown of the large protein molecules is greatly affected by purification or other treatment, and especially by the conditions of hydrolysis such as temperature, degree of acidity, or alkalinity and the length of time of hydrolytic action.[24]

Table 33. Amino Acid Content* of Gelatin

Per Cent	Amino Acids	Formulae
	(Monobasic monoacidic amino acids)	
25	Glycine, α-aminoacidic acid	$CH_2\,NH_2\,COOH$
8	Alanine, α-aminopropionic acid	$CH_3\,CH\,NH_2\,COOH$
<1	Serine, α-amino β hydroxypropionic acid	$CH_2\,OH\,CH\,NH_2\,COOH$
1	Phenylalanine, β-phenyl α-amino-propionic acid	$C_6H_5\,CH_2\,CH\,NH_2\,COOH$
8	Leucine, α-amino isocaproic acid	$(CH_3)_2\,CH\,CH_2\,CH\,NH_2\,COOH$
	(Dibasic monoacidic amino acids)	
3	Aspartic acid, α-aminosuccinic acid	$HOOC\,CH_2\,CH\,NH_2\,COOH$
6	Glutamic acid, α-aminoglutaric acid	$HOOC\,CH_2\,CH_2\,CH\,NH_2\,COOH$
	(Monobasic diacidic amino acids)	
9	Arginine, α-amino δ-guanidine valeric acid	$HN{:}C(NH)\,NH\,CH_2\,CH_2\,CH_2\,CH\,NH_2COOH$
6	Lysine, α-ε-diaminocaproic acid	$CH_2NH_2\,CH_2\,CH_2\,CH_2\,CH\,NH_2\,COOH$
	(Heterocyclic compounds)	
1	Histidine, α-amino β-imidazolepro-pionic acid	
20	Proline, α-pyrrolidine carboxylic acid	
12	Hydroxyproline, hydroxy-α pyrrolidine carboxylic acid	

* Approximate content based upon various sources.

Behavior of Gelatin. Good grades of gelatin are colorless, odorless, and tasteless. The dry material is of horny toughness and its specific gravity is 1.3. It has no melting point, but begins to soften with decomposition at 140°C. and burns with a characteristic odor, similar to burnt feathers.

It swells but is insoluble in cold water. Hot water does dissolve it,

[23] F. Krishnamurti and T. Svedberg, *J. Am. Chem. Soc.*, **52**, 2897 (1930).

[24] Proctor, *J. Chem. Soc.*, **105**, 313 (1914); Biltz, *Z. Physik. Chem.*, **91**, 705 (1916); Smith, *J. Am. Chem. Soc.*, **43**, 1350 (1921); Wintgen and Vogel, *Kolloid-Z.*, **30**, 45 (1922); Schryver, *Biochem. J.*, **17**, 487 (1923); M. Kunitz, *J. Gen. Physiol.*, **10**, 835 (1927); A. L. Ferguson, *Fifth Colloid Symposium Monograph*, 177 (1928).

and warm solution when cooled forms a gel which may be warmed again to form a solution (sol) again. The melting point of the gel is about 30°C. and the setting point of the sol is a few degrees lower, but neither is sharp. Agar gels melt at about 90°C. and set at 35°C. to 50°C.

Smith[25] postulates that there are two forms of gelatin: "A," the sol form, stable above 35°C., and "B," the gel form, stable below 15°C. At temperatures between 35°C. and 15°C. there is a mixture of "A" and "B," the proportions of each being dependent upon temperature and time. Above 35°C. a gelatin solution behaves like a typical viscous liquid, below 35° it changes its characteristics to that of a plastic solid.

If a solution of gelatin is made by heating it in water the gelatin will dissolve entirely as the "A" form and the viscosity on immediate cooling will be similar to that of a solution with much gelatin "A" and little gelatin "B." If the temperature is kept above 35°C. the viscosity will fall with ageing, except at the isoelectric point where it remains constant. At temperatures below 35°C. the ageing increases the proportion of "B" and viscosity rises, especially at the isoelectric point, and finally there is a gelation which is probably due to the formation of a fine molecular structure. This structure has been called a system of catenary threads.[26] Mechanical handling of gelatin sols may lead to increase or decrease in viscosity. Rapid random stirring will lower the viscosity, probably by destroying the solution structure. Slow uniform stirring may on the other hand increase the viscosity, probably due to an orientation of elongated particles assisted by this treatment. A fall of viscosity as a result of mechanical handling is reversible on standing, and may be due to a reformation of the solution structure.

As the gelatin concentration is increased, this solution structure becomes more pronounced. It is interesting at this point to note that as the concentration increases there is no crystallization in the usual sense as in crystalloids. The gelatin, on evaporation of its solution, holds tenaciously to the water, forming a continuous aggregation of protein molecules, and is obtained as a horny semi-transparent material. In order to dry it to a fine powder, it is necessary to use a dehydrating agent such as alcohol, acetone, or anhydrous sodium sulfate.

Gelatin gels are perfectly elastic for small stresses applied for short periods. The volume remains unchanged even for considerable deformation. The stress required to maintain a given deformation decreases with increase of the period of application of the stress, but does not become zero.[27] The finest grades of gelatin for food are made from calf skins

[25] Smith, *J. Am. Chem. Soc.*, 41, 135 (1919).
[26] Bogue, *J. Am. Chem. Soc.*, 44, 1313 (1922).
[27] A. W. Thomas, "Colloid Chemistry," McGraw-Hill Book Company, Inc., New York, 1934.

since the jelly strength of gelatin from this source is retained longer than for others.

Much of the behavior of gelatin is due to the sol ⟷ gel transformation and to the amphoteric nature of its molecular structure. Gelatin as

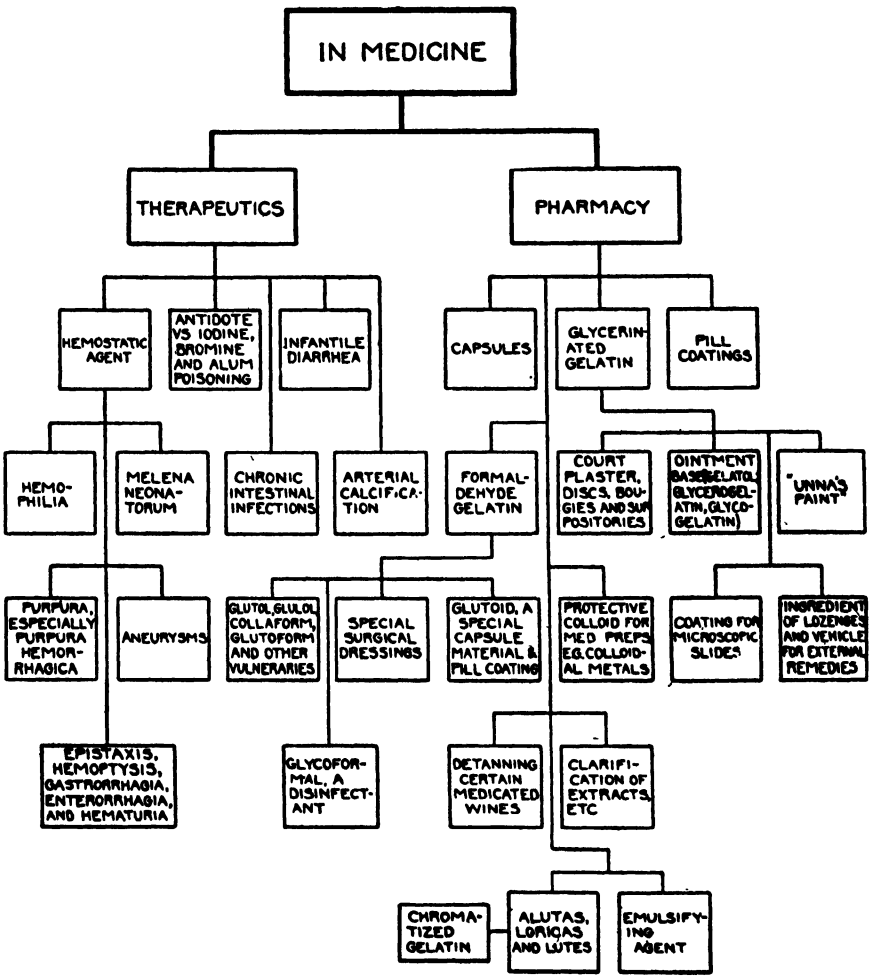


FIGURE 46. Uses of edible gelatins.

an ampholyte generally has an isoelectric point of 4.7 and combines with acid on the alkaline side and combines with bases on the acid side of its isoelectric point. Viscosity and osmotic pressure of gelatin sols show a minimum at the isoelectric point, rising to a maximum of different magnitudes on the acid and alkaline sides. Gelatin gels show a similar behavior

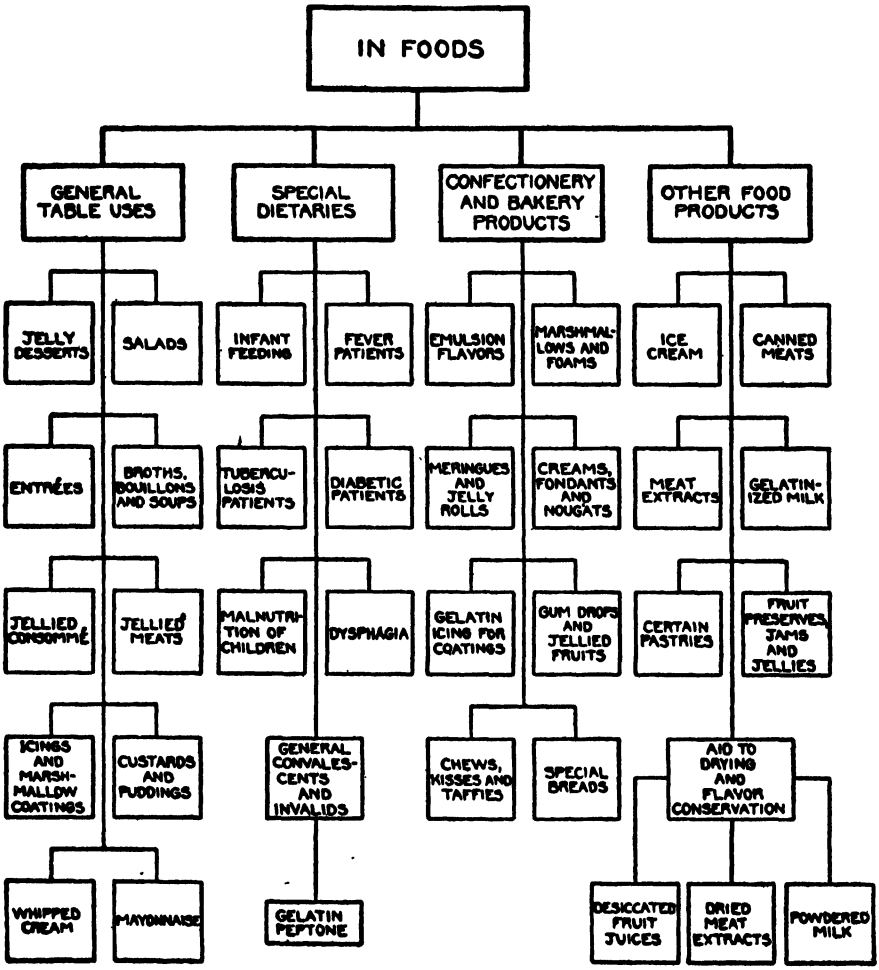


FIGURE 47. Uses of edible gelatins.

in properties, with a minimum at the isoelectric point and maximum at either side.

The principal uses of the edible gelatins are shown in Fig. 46 in medicine, in Fig. 47 in foods, and in Fig. 48 in miscellaneous applications, a chart prepared by T. B. Downey.[28] Major amounts go into jelly dessert powders, ice cream, and candy. In candies much is used for marshmallows. Cookies, jellied meats and certain dairy products account for large consumption of gelatin.

[28] T. B. Downey, *Ind. Eng. Chem.*, 15, 602 (1923).

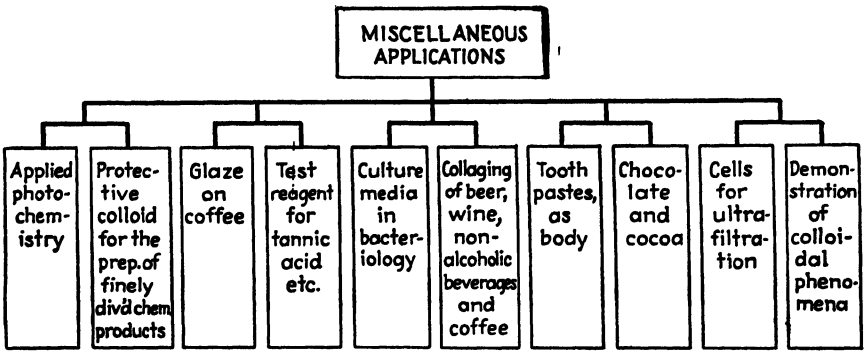


FIGURE 48. Uses of edible gelatins.

Inedible gelatin finds applications such as in sizing paper, textiles, and straw hats; capsules for pharmaceutical use; hectographs, a gelatin-glycerine composition and "Cerolagne" and "Carnesin" gelatin-wax display figures.

Photographic gelatin is prepared for photographic uses. It is made under careful supervision in order that each batch of gelatin is processed in a manner identical with the procedures producing a satisfactory sample. Mineral fat and microorganism content must be controlled. Appearance, non-turbidity, viscosity, setting point and melting point, pH, water content, and the influence on photosensitivity and fogging of the photographic silver salt emulsion are important characteristics considered.[29]

[29] H. Stadlinger, *Synthetic and Applied Finishes*, 4, 76 (June 1933).

Chapter 11

Gums in Cosmetics and Pharmacy

In the field of pharmacy and cosmetics the hydrophilic colloids are used because of their mucilaginous or oily nature and their properties of soothing enflamed or abraded membrane or skin areas and protecting them from irritation. They are often referred to as demulcents or emollients. They are suspending and emulsifying agents in creams, lotions, ointments, pastes, salves, face creams, and other cosmetic preparations. The property of the hydrophilic colloids of forming films upon evaporation along with their ability to be plasticised or softened by other components accounts for their presence in hair lotions, permanent waving compositions, bandoline, and wave-setting materials.

Gum arabic under the name Acacia is the first material in the Pharmacopoeia of the United States, the eleventh decennial revision. The same volume contains agar, gelatin under the name of Gelatinum, flaxseed or linseed under the name of Linum, the mucilages of acacia and of tragacanth under the name of Mucilago Acaciae and Mucilago Tragacanthae, and tragacanth under the name of Tragacanthae. The National Formulary of the Committee of the American Pharmaceutical Association, sixth edition, lists chondrus as well as the names of Irish moss and Carrageen, Dextrinum Album for white dextrin, also under the name of British gum, while a number of unofficial lists largely connected with the cosmetic arts include Cydonium or quince seed, karaya under names such as Indian tragacanth and Gum Sterculia, and other unofficial pharmaceutical listings include psyllium which is included in the British Pharmacopoeia Codex of 1923.

Acacia mucilage[1] is made by placing 350 g. of acacia or gum arabic in small fragments in a 1 liter bottle and adding distilled water in which 1 g. of sodium benzoate is dissolved, allowing the acacia to dissolve and making up to 1000 cc. Tragacanth mucilage is also made in proportions of 6 g. of tragacanth mixed with 75 cc. of hot distilled water containing 18 g. of glycerine. After complete solution, the mixture is diluted to 100 g. and strained.

[1] "Pharmacopoeia of the United States," 11th decennial revision, p. 238, 1936.

Redgrove[2] studied setting lotions made from psyllium seeds and found them less effective than those from quince seeds.

To prepare a decoction of psyllium seeds,[3] boil 1.5 parts of bruised seeds for 10 minutes with 120 parts of water, strain and make up to 100 parts by volume. To prepare the lotion, take 100 parts of this decoction, add rose or distilled water 100 and, carefully, perfumed alcohol, 100 parts. Tint with any suitable dye and perfume with any synthetic product soluble in weak alcohol.

Schwarz[4] gave formulae for the preparation of materials suitable for the care of the skin and hair, which formulae were founded on Irish moss, quince and psyllium seeds as well as tragacanth.

Redgrove[5] described setting lotions made from quince seeds with tragacanth.

A basic formula with tragacanth is: potassium carbonate 40 g., borax 10 g., mucilage of tragacanth 100 cc., alcohol, 100 cc., rose water to make 1000 cc. The mixture is also effective without the alkalies. Quince seeds, unlike tragacanth, produce a clear lotion with hot or cold water, and when of good quality are rich in mucilage. For a weaker, yet quite effective setting lotion use a decoction of quince seeds 25, alcohol 25, rose water 100 parts. Addition of terpineol or other special compound will enhance the odor. Alcohol must be added carefully to avoid precipitation.

Goodman[6] gives numerous formulae for hair curling fluid, hair set, finger wave, wave set based on acacia, chondrus, karaya, psyllium seed, quince seed, tragacanth, while others have suggested corresponding formulations employing alginates. The concentrations of the gums or hydrophilic colloids are of the order of 1 to 4 per cent, the most effective ranges appearing to be 2 to 3 per cent.

It is estimated that approximately 100,000 pounds of agar per year are used in laxatives and laxative emulsions while perhaps 25,000 pounds per year are employed in pharmaceutical emulsions of various natures.

Figg[7] studied psyllium seeds as a mild natural laxative in constipation. The mucilage test differentiates the worthless pale variety of seeds from the medicinal dark variety. Cover a small quantity of the seeds in a test tube with about 3 or 4 times their weight of water. After a short time only the dark seeds have swelled to a semi-solid mass which will remain in place when the tube is inverted.

[2] H. S. Redgrove, *Pharm. J.*, **130**, 29, 133 (1933).
[3] Decoctum Ispaghulae, *Brit. Pharm. Codex*, 1923.
[4] H. Schwarz, *Seifensieder-Ztg.*, **68**, 411, 422 (1941); *Chem. Zentr.*, I, 1316 (1942).
[5] H. S. Redgrove, *Pharm. J.*, **130**, 29 (1933).
[6] H. Goodman, "Cosmetic Dermatology," 1st Ed., McGraw-Hill Book Company, Inc., New York, 1936.
[7] H. B. Figg, *Pharm. J.*, **126**, 29 (1931).

Pin and Soung[8] studied the diuretic effect of psyllium seeds. Observations with three human cases revealed a diuretic effect characterized by an increased output of water, urea, chloride and uric acid.

Kober[9] suggested therapeutic preparations derived from psyllium seed. A pharmaceutical product suitable for promoting corrective tissue changes when used by injection is obtained from an aqueous suspension of the fatty acids of psyllium seed oil which are converted into water-soluble salts, as by treatment with dilute sodium hydroxide solution.

Gray and Tainter[10] investigated colloidal laxatives available for clinical use. These products can be classified into the following groups: colloidal clays, dried fruits, marine mucilages, acacia, tragacanth and psyllium. The latter two groups contain the most important products from the clinical standpoint. In distilled water the tragacanth preparations swelled to about 75 times the initial volumes, while the psyllium products swelled about half as much. In the presence of salt, hydrochloric acid and sodium bicarbonate, in concentrations comparable to those in the gastrointestinal tract, the increases in volume were reduced to about 20 times for the tragacanths and 15 times for the psyllium products. Tragacanth derivatives exert their laxative actions primarily through colloidal swelling, while purified psyllium products add to their lesser degree of swelling a mild direct irritant effect from their breakdown products.

Baron[11] suggested a bowel evacuant for use by rectal injection employing the hydrophilic colloids. A gelatinous material such as gelatin, agar-agar or gum tragacanth is dissolved in water, ox gall is dispersed in the material and the resulting mixture is added to glycerol to form a semi-liquid or sirupy product.

Knight[12] studied emulsions of petroleum oil for laxatives and made suggestions for modifications. Since the use of gum acacia (*A*) alone produces much smaller oil globules with liquid paraffin (*B*) than gum tragacanth (*C*) as used in the British Pharmacopoeia Codex, Knight recommends first making an emulsion with *A*, then incorporating *B*. Half the quantity of *A* prescribed would be sufficient. The use of 0.15 per cent benzoic acid is better than that of gum benzoin as a preservative. In the place of the expensive *C*, an *emulsio petrolei cum agar-agar* is recommended. Many modifications of petroleum oil and agar or other hydrophilic gums are widespread in daily use as mild laxatives.

Tice[13] described a new form of edible gelatin for specific application in

[8] King-Li-Pin and Woo-Ping-Soung, *J. physiol. path. gen.*, 32, 1144-7 (1934).
[9] P. A. Kober (assignor to G. D. Searle & Co.), U. S. Patent 2,115,491 and 2,115,492 (April 26, 1938).
[10] H. Gray and M. L. Tainter, *Am. J. Digestive Diseases*, 8, 130-9 (1941).
[11] L. Baron, U. S. Patent 1,621,186 (Mar. 22, 1927).
[12] W. A. Knight, *Pharm. J.*, 121, 297 (1928).
[13] L. F. Tice, *Drug Cosmetic Ind.*, 41, 191-3 (1937).

the pharmaceutical field under the name of Pharmajel. He suggested typical formulae for preparing emulsions and creams.

Kremel[14] suggested specific formulae for suppositories employing gelatin.

Redgrove[15] discussed the gums and gum substitutes in pharmacy and cosmetics while McGee[16] explored the field of gelatin as an emulsifier in pharmaceutical preparations.

Brown and Lum[17] give specific formulae for agar and paraffin emulsions. To obtain the best results, triturate sodium bicarbonate 10 grains, powdered tragacanth 20 and powdered acacia 60 grains to a smooth paste with glycerol 6 drachms. Dissolve agar 17.5 grains in boiling water 2 fluid oz., add this while hot to the mixture in the mortar while stirring. Then add liquid paraffin 3 oz., 2 to 3 drachms at a time. Triturate until cold, allow to stand for 1 hr., triturate again for 5 minutes and add water to complete 6 oz. If an emulsifying apparatus worked by hand is available, a thick emulsion is obtained with agar 15, sodium carbonate 6 grains, liquid paraffin 3 oz., tragacanth 5, acacia 5 grains, glycerol 2 drachms, water to make 6 oz. Nitardy, Berg and Georgi[18] gave manufacturing details.

Agar is dissolved in hot water and minute globules of emulsified petroleum jelly are dispersed in the solution while hot and the mixture is permitted to cool while quiescent.

In preparing liquid products containing agar in a quantity greater than that which would normally form a firm jelly in the presence of water, the agar is dissolved in hot water in the proportions required to form a firm jelly, and the solution is cooled and stirred to produce a semi-liquid mass of comminuted jelly particles and the latter are emulsified with a mixture of laxative oil and water.

Miller, Kurka and Chase[19] patented a medical composition of mineral oil, agar and lactic acid.

Lactic acid is used in such a proportion (suitably about 0.25 per cent or more with mineral oil 37.5 and agar 10 parts) that it is carried into the intestines to exert an inhibitive action on any toxic intestinal flora. Water, glycerol, sugar and other flavoring and preservative substances also are added, while Carter[20] incorporated milk sugar.

[14] A. Kremel, Austrian Patent 149,187 (Apr. 10, 1937).
[15] H. S. Redgrove, *Ind. Chemist*, 16, 145-6 (1940).
[16] T. D. McGee, *Australasian J. Pharm.*, 24, 61-2 (1943).
[17] C. L. M. Brown and E. A. Lum, *Pharm. J.*, 131, 341 (1933).
[18] F. W. Nitardy, F. F. Berg and P. Georgi (assignors to E. R. Squibb & Sons), U. S. Patent 1,913,561 (June 13, 1933). F. W. Nitardy (assignor to E. R. Squibb & Sons) U. S. Patent 1,799,804 (Apr. 7, 1925).
[19] G. C. Miller, J. F. Kurka and L. B. Chase (assignors to Kelp-Ol Laboratories), U. S. Patent 1,688,053 (Oct. 16, 1929).
[20] C. E. Carter, U. S. Patent 1,631,244 (June 7, 1927).

A composition for use in promoting growth of lactic acid bacteria in the intestinal tract comprises sugar of milk suspended in mineral medicinal oil and agar-agar.

Turrentine[21] suggested drying of kelp at a temperature below the boiling point of the plant juice for the production of a dehydrated product in assimilable form for therapeutic uses.

Skinner[22] gave practical notes on the preparation of ointment bases employing tragacanth as a dispersion agent.

An ointment primarily suitable for absorption is the following modification of the British Pharmaceutical Codex *Unguentum lanolini oleosum*: (A) Powdered tragacanth (No. 40) 2.5, (B) glycerol 20.0, water 100.0, (C) hydrous wool fat 250, (D) oleic acid 30.0 parts. Stir A with B and water to a smooth cream, heat to boiling and mix it into C previously mixed with D. Vegetable oils are good diluents, but coconut oil is regarded as a skin irritant.

von Neergaard[23] suggested the hydrophilic colloids as constituents in medicinal or candle shaped articles (bougies) for insertion in various openings of the body.

Bougies for the treatment of mucous canals and fistulas are prepared from silver nitrate or other water-soluble silver compound and substances which will swell and liquefy in contact with moist tissues, e.g., preparations of starch, tragacanth, agar, gum arabic, dextrin, gelatin, psyllium, laminaria, carrageen, quince mucilage, marshmallow and linseed. In order to increase the swelling action, sulfates, citrates, oxalates, sucrose, urea or weak alkaline substances may be added. Kieselguhr may be added to promote diffusion, and glycerol to give increased elasticity. Dyes and other substances also may be included. The compositions are preferably prepared in darkness.

Koenigsberger[24] suggested locust bean gum for a depilatory. A transparent base such as locust bean gum is used with a lithium-containing depilatory agent such as the reaction products of lithium hydroxide and hydrogen sulfide and with an inert gas such as nitrogen dispersed throughout the depilatory to form a material readily washed from the skin after use.

Bliss[25] discussed a tooth paste for children and suggested formulae with gums as binding agents. A satisfactory paste is made from very fine calcium carbonate and magnesium carbonate as mechanical cleansers

[21] J. W. Turrentine, U. S. Patent 1,513,298 (Oct. 28, 1925).
[22] H. Skinner, *Chemist and Druggist*, 112, 795 (1930).
[23] K. von Neergaard, British Patent 218,323 (June 30, 1923).
[24] F. Koenigsberger (assignor to Parfumerie St. Denis), U. S. Patent 2,031,489 (Feb. 18, 1936).
[25] A. R. Bliss, *Drug and Cosmetic Ind.*, 36, 409-10, 416 (1935).

with tragacanth as a binding agent, neutral glycerol, a blend of peppermint and anise oils with saccharin as a sweetening agent, while Klein and Kaplan[26] suggested an edible dentifrice containing gelatin and gums.

Okubo[27] suggested a tooth paste. A mixture of magnesium silicate, gum tragacanth, soap, glycerol and honey is dehydrated under reduced pressure and the product is mixed with boron oxide.

It is estimated that from 15,000 to 100,000 pounds of agar and alginates are used annually in the United States in connection with dental impression molds, particularly as substitutes for tin foil in processing acrylic dentures and as principal constituents of impression materials as well as denture adhesives. Molnar[28] has reviewed progress in this field.

Flack, Clarke and Tice[29] made a study of 64 different preparations employing gelatin and the sulfonamide drugs in an attempt to develop a dressing for burns which would embody the advantages and eliminate some of the disadvantages of a preformed film. The various modifications employed centered about 4 base formulae which are given; the most desirable is: sodium sulfadiazine 25, "Pharmagel B" (gelatin) 50, sulfadiazine 45, A-3 water (distilled water containing 0.52 g. methyl p-hydroxybenzoate and 0.28 g. propyl p-hydroxybenzoate per liter) 100 g. Thorough clinical evaluation was not accomplished, and definite conclusions cannot be drawn.

Wander[30] suggested a greaseless ointment base. An aqueous colloidal dispersion of a light-metal compound is mixed in the proportion of 1 or 2 to 3 at elevated temperature (60°) with a vegetable gel obtained from mucilaginous algae. The pH of the mixture is brought to about 6.5 by addition of an organic acid. The product is a homogeneous, ointment-like cream, suitable as a base for cosmetics.

A wound treating compound was suggested[31] in the form of a powdered product to stop the flow of blood and is made by transforming gum tragacanth into grains corresponding to a size of particles of 0.07 to 0.5 mm. and then causing them to swell a regulated amount by the limited action of acids or acid substances or salts of heavy metals, particularly zinc, tin, copper, chromium or oxidizing agents such as halogens or tanning materials.

Elsner[32] proposed products for blood-coagulation retarders which are

[26] H. Klein and E. Kaplan, U. S. Patent 2,154,168 (Apr. 11, 1939).
[27] S. Okubo, Japanese Patent 101,971 (July 15, 1933).
[28] E. J. Molnar, *Dental Lab. Rev.*, 18, 22-4 (1943); 19, 18-22 (1944).
[29] H. L. Flack, D. A. Clarke, and L. F. Tice, *J. Am. Pharm. Assoc.*, 34, 187-90 (1945).
[30] A. Wander A.-G., Belgian Patent 446,527 (Aug. 31, 1942).
[31] Lingner-Werke Vertriebs-Gesellschaft m.b.H. French Patent 833,863 (Nov. 3, 1938).
[32] H. Elsner, German Patent 667,279 (Nov. 8, 1938).

obtained by extracting carrageen or agar with water at about 20 to 25° with addition of a disinfectant, and evaporating the extract at below 50°C. The extract may be purified by dialysis before it is evaporated.

Gelatin is widely used in the form of sheets or as capsules for containers for pharmaceutical products. Thornley and Jones[33] suggested a hardening method employing formaldehyde which was commonly used, followed by a solution of thiosulfate to inhibit the secondary hardening process which gelatin undergoes on storing after treatment with formaldehyde.

Many of the gums have been used as adhesives to maintain the shape and form of therapeutic tablets. Wershaw[34] proposed gum arabic in connection with aluminum subacetate tablets. Coles, Barker, Robertson and Cowan[35] employed agar as a carrier for penicillin solution. A mixture consisting of equal volumes of a penicillin solution of twice the final concentration desired and 1 per cent agar in distilled water or isotonic sodium chloride solution is a suitable preparation for local treatment. Penicillin in the agar base remains active for at least a month at refrigerator temperature and diffuses rapidly from the agar when applied to tissues. Bartsch[36] used agar as an adhesive in nitroglycerine tablets for medicinal use. To 90 parts of lactose and 5 parts powdered agar-agar add a 10 per cent alcohol solution of nitroglycerin and dilute alcohol until the product can be granulated to go through a No. 15 sieve. Dry the powder, mix with 5 parts talc and pass through a No. 10 sieve; then compress it into tablets. Nitroglycerin is lost during drying and storage.

Hermann[37] patented an X-ray contrast composition for increasing the concentrations of suspensions such as barium sulfate for X-ray diagnosis. Preparations are described for suspensions containing 100 to 300 parts of barium sulfate, 1.4 to 4 parts of soluble salts of the acid contained in seaweed, algae, fuci, and kelp, and in some cases magnesium oxide.

Gresset[38] suggested compositions for skin treatment such as skin-rejuvenating compositions containing methyl cellulose, vegetable gelatin (agar), glycerol and water, with or without appropriate additions, such as pigments, waxes, or perfumes. The compositions melt at about 100 to 120° and solidify at about 35° to form a paste, which is removed from the skin after treatment.

Reviews of formulae employing sodium alginate in cosmetic prepara-

[33] B. D. Thornley and N. W. V. Jones, British Patent 561,204 (May 10, 1944).
[34] I. B. Wershaw (assignor to Dome Chemicals, Inc.,) U. S. Patent 2,371,862 (Mar. 20, 1945).
[35] R. B. Coles, A. N. Barker, E. A. Robertson and S. T. Cowan, *Lancet*, I, 720-1 (1945).
[36] O. Bartsch, *Dansk. Tids. Farm.*, 6, 229-41 (1932).
[37] S. Hermann, U. S. Patent 2,368,833 (Feb. 6, 1945).
[38] L. Gresset, French Patent 814,010 (June 14, 1937).

tions were made by Matthews.[39] Frydlender,[40] Jannaway[41] and Schwarz[42] gave a number of formulae for the use of seaweed colloids and the hemicelluloses as well as the natural gums in cosmetic preparations.

Helfrich[43] employed gum arabic in the formation of a cosmetic compact in which a "color vehicle" is formed of talc 99 lb., chalk 9 lb., and yellow ocher 15 oz. Eighteen lb. of the "color vehicle" is mixed with 100 cc. of mineral oil and with 1200 cc. of a dilute aqueous gum arabic solution and the mixture is used for making "wet-formed compacts."

Gum arabic was employed as a stabilizer in French preparations[44] in which a protective pomade or cream contains soap 19, gum arabic 4, lanolin 2, glycerol 1 and water 74 parts. Gum arabic may be replaced by dextrin and lanolin by other oily substances.

Zakarias[45] states that polysaccharide jellies (starch paste, glycerolated starch, gum tragacanth, etc.) can be preserved for a short time by the addition of considerable magnesium chloride. Zakarias has found that most of the magnesium chloride can be replaced by certain other inorganic salts (iron, sodium, calcium, chloride, etc.) which form loose adsorption compounds with the carbohydrate constituent of the jelly, rendering it both sterile and stable. Such jellies are employed for colloidal ointments and cosmetics in the manufacture of toilet soaps.

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[39] D. R. Matthews, *Pharm. J.*, **148**, 79 (1942).

[40] J. H. Frydlender, *Arch. droguerie pharm.*, **7**, 87-8 (Apr. 1939); *Chem. Zentr.*, I, 3329-30 (1940).

[41] S. P. Jannaway, *Perfumery Essent. Oil Record*, **35**, 185-90 (1944).

[42] H. Schwarz, *Seifensieder-Ztg.*, **68**, 411, 422 (1941); *Chem. Zentr.*, I, 1316 (1942).

[43] J. H. Helfrich, U. S. Patent 1,655,369 (Jan. 3, 1928).

[44] Compagnie Francaise pour l'exploitation des procedes Thomson-Houston, French Patent 692.757 (Mar. 26, 1930).

[45] L. Zakarias, *Parfumerie moderne*, **20**, 114-7 (1927).

Chapter 12

Gums in Paints and Coating Compositions

Water paints employing casein as a vehicle or binder are exceedingly old. Ancient Hebrew texts mention the painter and decorator who used soured milk, the important constituent of which is casein. Factory-made casein paints in powder form have been sold in the United States since the latter part of the nineteenth century.[1]

It is only in recent years after much development work that the hydrophilic colloids and modified celluloses began to find application in the paint industry. The hydrophilic colloids are alginic acid and its sodium and ammonium salts, and the modified celluloses are sodium carboxymethylcellulose, aluminum carboxymethylcellulose and hydroxyethylcellulose. They do not constitute a major ingredient in the formulation of the water paints, but nevertheless are of importance because of their stabilizing effects on emulsions of paints, waxes, and numerous other products.

They are utilized as thickeners, protective colloids, or as film formers themselves. As film formers with no modifying agents added, their use in the paint field is limited to a few special items such as binders in fire-resistant paints where the water-resistant property is not an essential requirement.

The Official Digest[2] states that the alginates and modified celluloses are best incorporated with an emulsion if, prior to this, they are dissolved and added as a solution. Since relatively small concentrations of the alginates and cellulose derivatives can be dissolved in water, their use in this manner is sometimes impossible, permitting only a small amount of water in the neighborhood of 5 per cent. In paints where the concentration of water is low, the protective colloid is best incorporated by grinding it directly into the paint. If this method is employed, care must be taken to insure proper dispersion throughout the emulsion since the cellulose derivatives are rather fibrous by nature and are not easily reduced in size in the grinding operation.

The solubility characteristics of the various celluloses must be taken into consideration in making up the solution or gel. Sodium carboxymethylcellulose, hydroxyethylcellulose, and ammonium and sodium algi-

[1] E. Sutermeister and F. Browne, "Casein, and Its Industrial Applications," p. 315, Reinhold Publishing Corporation, New York, 1939.

[2] *Official Digest Federation Paint & Varnish Clubs*, No. 250, 405-8 (Nov. 1945).

nate are soluble in hot or cold water, but more readily so in hot water. Methyl cellulose is soluble in cold and not in hot water. Aluminum carboxymethylcellulose is soluble in an alkaline medium.

It is suggested[3] that the dry powder be prewet with one of the solvents in the emulsion so as to aid the materials into solution. This prewetting prevents the formation of large agglomerates which are difficult to disperse.

Three viscosity grades of the cellulose derivatives and the alginates in three concentrations, 1, 5, and 10 per cent were compared. The solutions or gels were blended with several emulsions, the oil-in-water type in the ratio of one part of cellulose or alginate solution to four parts of emulsion (unpigmented). The oil-in-water emulsions used were alkyd resin emulsion, emulsifiable paint (Federal Specification T-1279 type), polyvinyl acetate emulsions, acrysol WA-5, and numerous others. These mixtures were then reduced 1:3 with water to note incompatibility. The emulsions were compatible with all the cellulose or alginate solutions taking the 1:3 reduction without throwing out. The mixtures could still be reduced in the same manner after standing one week, without breaking or separating. The ability of a stabilizer to aid in keeping the emulsion in its original phase is important, since oil-in-water emulsions often reverse to water-in-oil types upon long standing if they have not been properly formulated.

The addition of pigment often greatly affects the stability of emulsions, and influences the choice of protective colloid or stabilizer to be used. The choice of a certain cellulose derivative, alginate, or other protective colloid, depends on the properties desired in the emulsion and also on the constituents in the emulsion itself.

The alginates[4] have been incorporated in asphaltic paints and varnishes, shellac emulsions, and waterproofing compositions in an emulsified form.

Gum arabic[5] has been employed in paints as a glaze or varnish and for emulsifying oils.

Dextrin has been utilized to some extent in painting, but it is rarely used for emulsifying purposes.[6]

Bruhn and Timpke[7] propose the utilization of seaweed jelly in paint formulations.

[3] *Official Digest Federation Paint & Varnish Clubs*, No. 250, 405-8 (Nov. 1945).
[4] T. C. Gregory, "Uses and Applications of Chemicals and Related Materials," p. 18, Reinhold Publishing Corporation, New York, 1939.
[5] "First Report on Colloid Chemistry and its General and Industrial Applications," p. 53, British Assoc. for the Advancement of Science, His Majesty's Stationery Office, London, 1917.
[6] *Loc. cit.*, p. 52.
[7] H. Bruhn and C. Timpke, French Patent 381,323 (1907).

Clayton[8] found that gelatin emulsifies oils of both glyceride and hydrocarbon nature. Substances such as gum acacia, gelatin, casein, dextrin, agar, soap, and albumins act as emulsifiers by virtue of their ability to form colloidal hydrated compounds.

The gums also find application in coating compositions. Gelatin seems to be the one most employed, while the other gums are of lesser importance.

Murphy and Simmons[9] describe a coating composition comprising rubber and powders of good covering power prepared by mixing the powders with irreversible granular precipitates of rubber, etc., in any suitable paint mill. In the production of a white water distemper 150 parts of 60 per cent latex is added to 30 parts of sodium silicate dissolved in 30 parts of water. The granular precipitate obtained on dilution to a 5 per cent solution plus 24 parts of 5 per cent aluminum sulfate is stirred and allowed to stand over a filter cloth so as to obtain a creamy mass of 16 per cent concentration. A mix of zinc oxide 600 parts, china clay 500 parts, gum acacia 3.75 parts, aqueous ammonia (sp. gr. 0.880) 7.5 parts, water 985 parts, and the rubber precipitate 900 parts is made in a paint mill to uniform consistency.

Karaya gum was utilized by Manley and Wenzelberger[10] in developing a flexible coated fabric. An adhesive fabric consists of a backing fabric and a barrier sheet composed of the solids of a latex-rubber dispersion, e.g., 60 per cent latex 334 to 200 parts, karaya gum 160 parts, and clay 100 parts, deposited on and vulcanized to the backing sheet, and an adhesive coated on the barrier sheet.

Erdhal[11] describes a sizing and coating material composed of a colloidal solution of an algin base. The algin base is introduced into an acid bath such as 9 to 17 per cent sulfuric acid solution. The resultant precipitate is aged in the bath and the algin reaction product is collected.

A protective coating developed by Galakhov[12] consists of a water glass of 55 to 60° Bé. mixed with an adhesive such as dextrin, tripoli, finely powdered pigment, and a previously prepared mixture of mineral oil with lime powder or a similar base.

A coating composition[13] comprises an aqueous solution of a binder consisting of a protein glue or a water-soluble gum, and a flexibilizing

[8] W. Clayton, "The Theory of Emulsions and their Technical Treatment," P. Blakiston's Son & Co., Philadelphia, Pa., 1928.

[9] E. A. Murphy and D. N. Simmons (assignors to Dunlop Rubber Co. Ltd.), British Patent 391,973 (May 11, 1933).

[10] F. N. Manley and E. P. Wenzelberger (assignors to Johnson & Johnson Ltd.), Canadian Patent 423,421 (Oct. 24, 1944).

[11] B. F. Erdhal, U. S. Patent 1,625,301 (April 19, 1927).

[12] P. G. Galakhov, Russian Patent 44,619 (Oct. 31, 1935).

[13] Atlas Powder Company, British Patent 495,352 (Nov. 11, 1938).

agent such as sorbitol. The ratio of binder to the flexibilizing agent is not greater than 9 to 1 and not less than 1 to 3. The binder may be gelatin or proteins, dextrin, acacia, tragacanth, or karaya. The agent may be sorbitol alone or in an admixture with glycerol or lower polyhydric alcohols. The compositions may also contain linseed or mineral oil, sulfonated castor oil, hardening agents such as formaldehyde (CH_2O), $(CH_2O)_x$, and alum, and a preservative or antimold ingredient such as copper sulfate, β-naphthol, or sodium benzoate. The compositions may be used as adhesives, as oil-proof protective films, or impregnants for pressed paper pulp bottles or for woven fabrics, as paint for concrete, as a varnish for artificial leathers and as a coating.

May[14] describes a coating composition made by mixing a solution, in an organic solvent that is nonmiscible or of limited miscibility with water, of one or more substantially water-insoluble materials of the type of resins, natural or artificial rubber, chloro-rubber, and other rubber derivatives, cellulose esters, and ethers, with an aqueous precipitant. This forms an emulsion or dispersion, wherein a quantity of an organic substance capable of swelling in water and forming a colloidal dispersion in water such as gelatin, is incorporated. A sufficient quantity of a wetting agent is added to stabilize the emulsion or dispersion. The quantity of the substance capable of swelling in water is less than would be required for the stabilization of the emulsion in the absence of the wetting agent.

A composition for forming a continuous film and suitable for coating paper was developed by Van der Meulen.[15] It is prepared from casein or gelatin and contains a water-insoluble salt of a sulfonated vegetable oil in a state of submicroscopic dispersion, and water, in a proportion of 1 to 5 parts for each part of the base material.

Boyce[16] describes a coating composition for use on paper, pulp board, wood, etc. A transparent film is formed which contains gelatin and the reaction product formed by heating glycerol for three hours with a molecular proportion of phthalic anhydride at about 280°.

A painting or coating material developed by Maeda[17] consists of glycerol, formalin, gelatin, salicylic, and acetic acid which is added to a hot solution of carrageen.

Metallic bodies[18] are coated with several thin films of a material com-

[14] W. May, British Patent 514,037 (Oct. 30, 1939).
[15] P. A. Van der Meulen (assignor to John R. Ditmars), U. S. Patent 2,152,829 (April 4, 1939).
[16] C. M. Boyce (assignor to John R. Ditmars), U. S. Patent 1,978,406 (Oct. 30 1935).
[17] T. Maeda, British Patent 361,805 (April 22, 1931).
[18] R. P. Dinsmore (assignor to The Goodyear Tire and Rubber Co.), Canadian Patent 307,702 (Jan. 13, 1931).

prising gelatin and polyglycerol, each film being subjected to the action of alum formaldehyde and other tanning agents. This coating composition is used for the joints of sectional bodies.

Wendt, Eggert, and Trautmann[19] increased the viscosity of gelatin solutions by such compounds as 1-stearoylaminonaphthalenedisulfonic acids and 1-palmitoylaminonaphthalenedisulfonic acids. The solutions are used for coating compositions.

[19] B. Wendt, J. Eggert, and G. Trautmann (assignors to General Aniline & Film Corp.), U. S. Patent 2,265,463 (Dec. 9, 1942).

Chapter 13

Gums in Textile Operations

The application of water-soluble gums of hydrophilic colloids must be considered from the viewpoint of their properties and the differing methods of utilizing them, first, in connection with fibers such as cotton, rayon, and wool, and secondly, from the section of the manufacturing operations such as those pertaining to weaving where the preparation of yarns for the loom employs gum, where the decoration of the fabric as in printing requires thickeners, and where the cloth which is being processed requires additive properties imparted to it by finishing agents.

For the preparation of yarn for the loom in operation, often referred to as "slashing," the cotton industry employs starches, carbohydrates, and the plant exudation gums. In the same operation, the rayon industry prefers water-dispersible proteins, such as gelatin. The woolen industry requires less of yarn preparation for weaving, and when yarn sizing is done glue satisfies the requirements.

Nylon yarn is commonly sized with compositions formulated around polyvinyl alcohol. The fibers of casein, and related proteins, particularly those of a synthetic nature and usually employed in blends with rayon, are sized in a manner similar to that of rayon. "Rayon" designates the group of synthetic fibers made of regenerated cellulose by the viscose, cuprammonium and nitrocellulose processes as well as cellulose acetate in its ester or in its saponified and regenerated form.

The water-soluble gums are usually furnished to the textile industries in the form of lumps or powders, but also as solutions or as processed or unprocessed constituents of proprietary preparations. Locust bean, arabic, karaya and tragacanth gums are used in the largest amounts, while Irish moss and sodium alginate are also finding application. Considerable research has been carried out on the preparation of textile fibers from alginates.

The literature on gums in textile manufacture contains contradictions even among experts, since many of the formulations are secret and the expert frequently is either limited to practice in a few mills or does not wish to reveal "secrets."

Where a careful balance of formulation and techniques to give optimum results within allowable production costs has been achieved, many textile

plants have also worked out substitutions of gum materials depending upon varying market prices and other factors so that formulations have a degree of flexibility.

It is important to obtain, as far as possible, uniformity and homogeneity of the gum solutions. Foreign matter must be largely removed and solutions must be strained, sometimes several times during their preparation in order to remove insolubles.

Gum arabic, gum Senegal, gum gedda and related gums sold to the textile industries as tears and powders, serve as thickening agents in printing, in silk finishing, and as "body builders" in transparent finishes for rayon. Objectionable stiffening may be broken down by mechanical processing. For cotton finishing the cost of the gums is generally prohibitive and starch and British gum are employed.

Although gum arabic is ordinarily completely soluble in water, some of the inferior grades in the Acacia group, such as those from India, Australia and the Cape, contain a fairly high proportion of insolubles which swell to form a sticky, gelatinous mass. A good textile gum[1] should be completely soluble in equal parts of water to give a clear, light colored solution which is not coagulated after one week when mixed with various metallic mordants or tannic acid. For complete solution some qualities require boiling water or boiling water and pressure or the addition of organic acids. Frequently, despite complete solubility and good clarity, a gum solution does not apply well and it is therefore necessary to make a practical application test.

Arabic mixes well with strongly alkaline solutions and strong organic acids and may thus be used for all kinds of discharges (removal of color so as to form white patterns on colored backgrounds) and resists (protection of areas of design of the fabric against the adherence of color), and for indigo printing. In practice, however, they are often replaced in these by the cheaper British gums, tapiocas and modified starches.

In making up arabic solutions, the gum is stirred in cold water for some time, after which floating bits of wood and other foreign matter are skimmed off the surface, the solution is heated for several hours with continuous stirring in a jacketed tank and allowed to remain undisturbed for several days to permit settling of sandy material, some of it exceedingly fine. The solution is then strained and is ready to use.

Arabic when mixed with solutions of starch, flour, tragacanth or some of the other gums causes these to lose their body and become slimy and unusable. The colloid chemistry of this phenomenon has been discussed under the heading of coazervation in the chapter on gum arabic. Ac-

[1] E. Knecht and J. B. Fothergill, "The Principles and Practice of Textile Printing," 3rd Ed., Charles Griffin & Co. Ltd., London, 1936.

cordingly, arabic and the related gums of this class are best used alone, though sometimes they are added to a starch or flour paste to soften and thin printing colors that are too stiff.

In printing with vat or insoluble colors, the dyestuff is incorporated in the printing gum as an insoluble pigment. In order to color the fiber or fabric in a form fast to light, the dye must be reduced by chemical agents to a soluble condition. The dyestuff could be made soluble and then mixed with the printing thickener. For the best results and the optimum fixation in printing, this solution and reduction must take place after the printing operation in the step of "ageing" or treatment in steam after printing. Accordingly, printing paste formulae for vat printing include the insoluble dispersible dyestuff, the thickener or combinations of them as carriers for the dyestuff to hold them in place, and chemical reducing agents to solubilize the dyestuff. The thickener preferably should not enter into chemical combination with the other constituents of the printing paste, and for most efficient utilization of the dyestuff so that minimum amount gives maximum coverage, should not cause agglomeration of the particles of dispersed dyestuff.

The dyestuff reducing and solubilizing agent should be one whose speed of reaction is controlled by temperature and amount of moisture. Materials of this type can be obtained whose reaction rate is slow at room temperature but very rapid at temperatures of steam, particularly saturated steam. Sodium sulfoxylate formaldehyde is the preferred reagent. A widely used printing paste would have the formula given below:

4 parts dispersible dyestuff
6 parts glycerol
10 parts water
53 parts British gum and arabic thickener
15 parts potassium carbonate

The dye and the glycerol are mixed together, the potassium carbonate dissolved in water and added to the dye paste. The mass is heated to 140° and the thickener then added. After being kept at 140° for 15 minutes or until a uniform paste is obtained, the mass is cooled and 6 parts of sodium sulfoxylate formaldehyde in 6 parts of water is added. The material is strained and used as a stock dye paste. In application it is thinned with a dilution material which contains no dyestuff whose formulation is 60 parts British gum and arabic thickener, 5 parts potassium carbonate, 0.6 part sodium sulfoxylate formaldehyde, and 34.4 parts of water. This paste may be mixed with the color paste in any proportion to give lighter shades.

According to Knecht and Fothergill[2] arabic and similar thickenings give even and transparent shades. For this reason arabic thickeners are mainly employed for printing light colors, particularly those which form the ground or blotch of the pattern. The colors on the fabrics after washing, however, are lighter in shade than when modified starches or tragacanth are used. In other words, the arabic pastes tend to give lower color yields or lower efficiency of dyestuff utilization. In order that sufficient viscosity and body be imparted to the printing paste, arabic must be employed in concentrations of the order of 30 to 50 per cent. The amount of gum and the high solids content do not allow the dyestuff to penetrate very deeply into the cloth. Too much of the dyestuff is held in the surface layer of thickener. As a result, when the goods are washed and the surface layer of thickener is dissolved, considerable dyestuff held in the thickener is lost to the wash-water and is thus wasted. This color contaminates the wash-water. If very strong dark colors are printed with arabic thickenings, the large amount of color dissolved out during the washing of the pieces affects the brilliancy and purity of any other colors that might be associated with them. The colors and mordants used in textile printing are susceptible to the soiling action of any highly colored wash-waters through which they may have to pass.

Karaya is sold to the textile industry chiefly powdered or in a solubilized form as a powder, paste or solution. Its principal use is as a thickening agent for printing pastes.

Since karaya does not dissolve in water but swells to form a gel, it must be ground fine before mixing with the water and then, for best results, boiled under a slight pressure to bring it into a solubilized form. A method of solubilizing the ground gum is by boiling with small quantities of oxidizing agents as sodium peroxide or persulfate. The mucilage so formed is decolorized sufficiently for use as a thickening agent for printing. For finishing of textiles, it may be completely decolorized by further treatment with bleaching powder (calcium hypochlorite or chloride of lime). A method for solubilizing karaya is as follows: Stir 100 kilos ground karaya gum in 250 liters cold water for 1 to 1½ hr., and adding 0.3 kilo sodium peroxide, then add and stir in well for ½ hr., 0.3 kilo sodium peroxide and 20 liters water, raise to a boil and continue boiling for 3 hr., cool, neutralize with hydrochloric acid (if necessary) and make up with water to 500 liters. It is claimed that at this strength the karaya solution is equal in thickness to a gum Senegal or arabic solution of 400 grams per liter, is cheaper, and is suitable for all purposes to which the latter is put in printing.

[2] E. Knecht and J. B. Fothergill, "The Principles and Practice of Textile Printing," 3rd Ed., Charles Griffin & Co. Ltd., London, 1936.

Several of the insoluble gums, like karaya and inferior grades of arabic, are solubilized and sold as paste or in dry form. The insoluble gums are used by screen printers and also for finer cotton printing. With all classes of work they give an exceptionally sharp mark, do not stick to the copper rollers, produce practically no foaming, yield bright, transparent colors and wash out easily. Such prepared gums with a solids content of about 30 per cent have better body than arabic of 50 per cent concentration. Prepared gums of 50 per cent solids content give pastes of good consistency so that the color mixer has ample leeway in dissolving his dyestuffs, since these gums thin down more slowly than arabic. Their other advantages over arabic are that they are less expensive and are free from grit and are uniform, requiring no straining or settling. Freedom from grit reduces scratching and doctor blade troubles.[3]

Locust bean gum generally comes to the textile industry in powdered form, in solution and as a constituent of proprietary compounds. The powder generally consists of finely ground decorticated seeds of the locust bean, with most of the residual husk removed by screening but still containing the germ. Presence of the germ promotes fermentation and the mucilage becomes thin and watery. Powdered locust bean in which the germ has been removed, e.g., "Tragon," is also available. Solutions of locust bean gum of about 5 per cent concentration are widely sold to textile mills; the solutions in some cases are germ-free, e.g., "Tragasol," and in all cases contain a preservative such as phenol to retard decomposition.

Locust bean gum is applied in printing pastes, in sizing, and in finishing white and printed fabrics because of its good binding power, transparency and flexibility. In printing it finds use as a thickener in the printing with diazo-solutions, acid resists, and acid colors on wool and silk. Working qualities are similar to tragacanth but colors are brighter and fuller. It is suitable for chrome colors on cotton, leaving them very soft. It is used for printing cotton draperies, dress goods, and all classes of work not calling for a too definite outline. When locust bean gum is used in admixtures with starches, British gums, or dextrins, removal of these by washing is assisted and does not reduce sharpness of mark. Although easily removed in washing, it is suitable for work that may not be washed, for example, screen printing, yarn and warp printing.[4]

A special use for locust bean gum is in connection with the application of vat colors by spraying and screen, block, and roller printing. It is also used in some types of waterproofing since the gum reacts with lead and aluminum acetates and bichromates to form water-resistant films.

[3] T. R. Harris, *Am. Dyestuff Reptr.*, 17, 95 (Feb. 6, 1928).
[4] T. R. Harris, *Am. Dyestuff Reptr.*, 17, 95 (Feb. 6, 1928).

Locust bean gum mucilages are best prepared by sprinkling the gum lightly into cold water, which must be stirred continuously to prevent the formation of lumps. The gum swells up quickly and forms a somewhat granular-looking paste. When all the gum has been added and thoroughly incorporated, it is boiled until it thickens and becomes smooth and homogeneous. It is then strained to remove foreign and insoluble material.

Locust bean gums possess unusual thickening power; good qualities are 2½ to 3 times stronger than tragacanth in thickening power and consequently are much cheaper than the latter where applicable. Alkalies and tannic acid convert locust bean gum into ropy masses and its use in mixtures with metallic mordants is not always satisfactory. Addition of acetic or other organic acids to mixtures containing tannic acid and metallic mordants improves the behavior of the gum.

Tragacanth, because of its high price, has been displaced in many of its textile applications by other gums, particularly locust bean gum and karaya. It comes to this market chiefly in the form of dry, horny scales, as a thick paste of 8 to 10 per cent concentration, and as a constituent in proprietary compounds.

Tragacanth finds use as a thickening agent with vat dyes in the pigment pad method, to some extent as a binding agent to assist in preventing dusting of backfilling mixes carrying heavy mineral fillings. It is also used to some extent as a finish on mercerized shirtings owing to its transparent film which does not appreciably reduce the lustre.

Tragacanth does not dissolve in water but swells to give a thick paste, and a good gum will form a thick smooth paste with at least twenty times its weight of water. On boiling, the mucilage becomes thinner and smoother and even the commercially purchased 8 to 10 per cent pastes must be boiled and stirred to assure homogeneous dispersion, otherwise gel spots on the yarn or fabric may occur. When boiled under pressure, the mucilage becomes very thin.

Tragacanth varies in its behavior towards tannic acid, metallic salts, and alkalies. The best gum for textile printing does not become gelatinous with these substances. Most qualities will mix fairly well with dilute alkalies, though curiously enough, the best quality is converted into a ropy mass by strong solutions of caustic soda, whereas the cheaper quality can frequently be mixed perfectly with soda sufficiently strong to discharge tannin mordants. There is variation in behavior of shipments of different seasons towards alkalies.

In making tragacanth mucilages or thickenings, the gum is soaked in water until it is swollen up into a thick paste, boiled and stirred continuously in a jacketed tank until homogeneous, cooled and strained.

Tragacanth is used in printing as a thickener, either alone or in combination with starch. It is especially useful in printing dark, heavy blotches since it is easily removed by washing the cloth, leaving the latter almost as soft as it was before printing. For pale blotches or grounds for wool printing and for work where softness of feel is important, tragacanth finds use. It is mixed with albumen in making pigment printing colors and enters into a good many of the dye liquors and preparations that are padded on the mangle. In the latter it tends to equalize the absorption of the liquors by the cloth and insures level padding. The tragacanth thickening used for ordinary blotch printing is of about 4 to 5 per cent concentration.

Although the gums find many uses in the textile industry, starches and dextrins find much greater use in the same applications than the gums, and frequently the gums are used as a supplement to the starch, chiefly to toughen the starch film.

Starches find their greatest use in textiles in warp sizing, printing paste thickeners, and finishes, especially on cotton. All cheaper commercial forms of starch are used such as corn, potato, tapioca, rice, wheat, sago, and sweet potato starch. Both domestic and foreign sources of these are employed and very often the mills in an area use the particular kind of starch that is produced locally. There are two types of starch used, the regular pearl variety or "thick boiling," and "thin boiling" starch, the latter produced from corn starch through chemical modifying processes. The thin boiling starches are sold on the basis of the fluidity (reciprocal of viscosity) of their solutions.

For printing pastes, wheat starches are the most commonly used starch thickeners. A stable thick paste has 5 to 10 per cent solids content. It does not tend to get thin and watery as does potato starch and is clearer than corn starch. Other starches and wheat flour are also used. Where cheaper fabrics are printed and softness of finish is not a factor, starch is satisfactory, but in higher grades of printing where price is of less importance and brilliance of shade and penetration are the chief requisites, better results are obtained with the gums.[5]

Another disadvantage of starch pastes is that they set to a stiff nonadhesive mass with alkalies. As a consequence, mixtures and other thickeners with the starch are used for vat, naphthol, and other alkaline printing pastes. Starch pastes are not washed out by a simple soaping as are British gums and natural vegetable gums. The starch must be treated with enzymes to solubilize it.

British gums give clear pastes but their solids content is high, 50 to 60 per cent, and penetration of dye is diminished. British gums are easily

[5] T. R. Harris, *Am. Dyestuff Reptr.*, 17, 95 (Feb. 6, 1928).

dissolved, making formulation and removal simple. They are not adversely affected by alkalies, dyes, and mordants.

Sizing

Sizing or slashing consists of the treatment of warp threads with a solution that forms a thin layer of binding material on the yarn in order to hold together all loose fibers or filaments and strengthen the yarn for weaving.

Sizing formulations are often judged as to their quality by abrasion tests on the yarns, those sizes which show the greatest resistance to abrasion and chafing being considered as superior. Warp sizing is a very important operation in cotton textile plants where the margin of manufacturing profit is small, in that weave room production and weave room costs can be affected to the extent of 25 per cent by the performance characteristics of the sizing materials. In cotton "slashing" or sizing, various forms of starches constitute the bulk of the sizing materials but gums are added to toughen the starch film. This toughening increases the strength of an individual strand of the yarn and also helps lay down the protruding whiskers of fibers. Some authorities state that the gums also act as binders to hold the fibers closer to the core of the yarn. Mixtures of starches and gums give superior performance to those of starches alone, while the gums alone ordinarily would be considered too expensive.

Filling yarn is not sized, but all cotton warps, rayon warps, and part of the wool warps are sized.

Hart[6] points out that warp yarns are sized to give strength to the yarn by cementing the individual fibers together to protect them from being rubbed up again during weaving. Unsized yarns under tension break partly by actual breakage and partly by their slipping apart. In the sized yarn the cementing effect of the size and its surrounding film causes the sized yarn to act more as if it were a single large solid fiber. Besides adding strength, the size gives greater compactness and smoothness to the yarn to reduce the frictional resistance. As a consequence, sizing cuts down breakage during and after weaving and so increases production and keeps down costs, at the same time improving quality.

A good size must have other desirable characteristics as well, some of which are specific to the type of fiber and the character of the finished fabric. It should be readily removable in the desizing or boil-off operation and leave the fabric with the desired feel. In some cases the weight and hand of the fabric before the boil-off is of importance and the sizing must contribute to the desired properties of the fabric.

The ingredients in sizing agents fall into the following groups:

[6] R. Hart, *Am Dyestuff Reptr.*, **25**, 231-6 (1936).

1. Adhesives, e.g., starch, flour, gums, dextrin, gelatin (for rayon).
2. Softeners, e.g., fats, waxes, oils, e.g., castor oil, coconut oil, palm oil, Japan wax, paraffin wax, spermaceti, stearin, vegetable tallow, hydrogenated fats and oils.
3. Penetrants, e.g., sulfonated oils, soaps, higher alcohol sulfates.
4. Preservatives, mildew preventives, etc., e.g., phenol, sodium silicofluoride, salicylic acid, cresylic acid, salts of benzoic acid.
5. Inert loading agents, e.g., china clays, talcs. Used where added weight and body are desired.
6. Fugitive dyes or tints to identify warp yarns of different twists such as S and Z in wool crepes and coatings.
7. Modifying agents, e.g., magnesium or calcium chloride (for cotton) which acts as a deliquescent agent, a preservative and foam-inhibitor.

The "adhesives" in group 1 are the "starches and gums" but there are serious objections to such terms. The materials are more than adhesives. They impart to the size the required body and viscosity and hold in suspension softeners and inert loading agents. They give strength by binding the fibers together, by their own cohesive strength, and by giving smoothness to the surface of the yarn. A better term for the group would be "organic emulsoid colloids."

The principal gums used in cotton sizings in order of importance are locust bean, karaya, tragacanth and arabic, the last to a limited extent. In rayon, gelatin is preferred, while arabic, tragacanth, locust bean and Irish moss are used but little. Not all wool warps are sized since many manufacturers prefer no size. Others employ sizes containing glue or starches or combinations of starches and glue. There is great secrecy as to the compositions of sizing formulae for wool weaving.

All cotton warps are sized. Most starches, especially the cheapest varieties, are used, including those of corn, potato, tapioca, rice, wheat, sago, and sweet potato. Textile mills frequently use a starch that is produced locally or close by, but many mills use starches from distant areas and much imported starch finds use in the United States. Thick-boiling and thin-boiling starches, flour, British gums, other dextrins and the natural gums make up the list of the "adhesives" for cotton warp sizing. Most cotton sizes contain starch and even those that contain gums (other than arabic) usually also contain starch, the gums adding to the toughness of the starch film. Locust bean gum is used more than other gums in cotton sizing. Karaya gum is second in importance.

A good size must be easily removable when it has served its purpose. After the yarn is woven into cloth, the gray goods must be made ready for other operations: for example for cotton, bleaching, sometimes merceriz-

ing, dyeing and finishing; but first it must be desized. For cotton, the gray goods as received by the bleachery are generally first singed to burn off the hair or fuzz and then passed to a quench box containing water to extinguish any sparks. The box often also contains an agent to solubilize the warp size. The desizing agent may be ½ per cent sulfuric acid or one of several types of enzymes. In many plants the desizing operation is carried out in the kier boil. The desizing agent is one of several organic compounds containing chlorine which gives a mild bleaching and oxidizing action as well as a desizing action. "Activin," the sodium salt of chloroparatoluene sulfonamide, is an important compound for desizing in the kier. Size and desizing agents are washed out of the fabrics in the succeeding operations.

Some typical cotton sizing formulations[7] containing gums are given as examples. Size formulae are legion and numerous variants are in commercial use.

TYPICAL GINGHAM SIZE FORMULA

(*Makes 125 gallons of cooked size*)

Water	100 gal.
Potato or corn starch	80 lb.
Softener A (see below)	5 to 5½ lb.

Mixing directions:—Mix starch with cold water for 20 minutes, bring to a boil in ½ hr., add softener A and continue to cook 1¼ to 1½ hr. Softener A contains saponifiable fats (tallow base), 4 per cent locust bean gum and sufficient calcium chloride to act as a preservative and reduce the tendency of the size to foam. Moisture content is less than 10 per cent. The product is soluble in hot water and starch solution.

TYPICAL SIZE FORMULA FOR 8 OUNCE DUCK

(*Makes 110 gallons of cooked size*)

Water	95 gal.
Corn starch	120 lb.
Softener A (see above)	10 lb.

Mixing directions:—As given for gingham size.

TYPICAL CHAMBRAY SIZE FORMULA

(*Makes 140 gallons of cooked size*)

Water	115 gal.
40° F.L. Starch (see below)	110 lb.
Softener A (see above formula)	5½ lb.

Mixing directions:—Mix the starch with cold water for 20 minutes, bring to a boil in ½ hr., add softener A and continue to cook 1¼ to 1½ hr.

40° fluidity (F.L.) starch formula (makes 150 gallons of cooked size): Mix 115 lb. thin boiling starch with cold water for 20 minutes, bring to a boil in ½ hr., add 5½ lb. of softener A and continue to cook 1¼ to 1½ hr.

[7] G. R. Merrill, A. R. Macormac, and H. R. Mauersberger, American Cotton Handbook, American Cotton Handbook Company, New York, 1941.

TYPICAL SIZE FORMULA FOR A FINE COUNT FABRIC MADE FROM 35S C.P. YARN

(*Makes 130 gallons of cooked size*)

Water	98 gal.
Potato starch	88 lb.
Softener D (see below)	9 lb.
Locust bean gum	7 lb.

Softener D is a combination of tallow, locust bean gum and sulfonated oil with about 20 per cent moisture content.

TYPICAL FORMULA FOR GAUZE SIZED ON A HIGH SPEED SLASHER

(*Makes 150 gallons of cooked size*)

Water	100 gal.
Potato starch	60 lb.
Locust bean gum	3 lb.
Softener D (see above)	6 lb.

Mixing directions:—Mix starch, gum and cold water for 20 minutes. Bring to a boil in ½ hr., add softener and cook at a boil for 1½ hr.

TYPICAL FORMULA FOR TICKING SIZE

(*Makes 240 gallons of cooked size*)

Water	210 gal.
Corn starch	165 lb.
Enzymic starch converter	1 lb.
Unsaponifiable waxes and oils	9 lb.
Locust bean gum	12 lb.

Mixing directions:—Mix starch, water, and gum and converter with water. After mixing 20 minutes, bring to a boil in ½ hr., add waxes and oils and continue to cook for 1½ hr.

Sizing formulae for rayon are generally on a gelatin basis, the gelatin being of the technical grade and serving as the major adhesive constituent in the size. The concentration of the gelatin in the size is ordinarily varied as to whether acetate warps or viscose yarns are being slashed, as well as their density in numbers per inch, their denier size, the weaving speeds in the number of picks per minute on the loom, and whether the warp is of filament yarn or of spun yarn. A range of formulations is given below:

50 gal. of soft water
6 to 22 lb. of 175 to 300 g. technical gelatin
2 to 8 lb. of softener, being a mixture of sulfonated olive and coconut oil as a blend
0 to ½ lb. penetrant
0 to ¼ lb. anti-foam agent
¼ lb. preservative such as cresylic acid, chlorinated substituted phenol or the like.

The gelatin is allowed to swell and is brought into solution with hot water, preferably not higher than 160°F.

Gelatin has been used for many years in the slashing of rayons, but it

is only in recent years that a definite procedure or technique has been developed instead of the trial and error method of the past. Any substance which is deposited on or impregnated in the yarn during slashing must be removable easily and economically. Gelatin was found to come closer to meeting this requirement than most other products. While use of animal gelatin has been increasing, starch has also been finding a place for itself in combination.

Boiling point temperatures during the boil-off damage spun-rayon fabrics, but when gelatin is used in the slashing operation, the temperatures may be lowered, as gelatin can be removed readily. Several starch manufacturers have developed a highly soluble, low-temperature starch, which when blended with gelatin is found to be compatible.

In sizing acetate yarns, higher concentrations of gelatin solution are needed than for viscose yarns because the acetates are more water repellent. These two types of yarn differ substantially in requirements of jelly strength in the gelatin used. Viscose requires a much lower jelly strength than acetate. The principal factor in any such slashing solution is the balance between the softener and the adhesive. Customary practice is to use one pound of solution to every pound of yarn in the warp. A factor which influences gelatin sizing concentrations in slashing is the type of material for which it is intended. The exact amount of sizing protection offered by the gelatin needs to be carefully evaluated.

It was discovered that a gelatin glue of high quality materially strengthened the sized material, but greatly reduced its elongation. When the concentrations were reduced to promote greater penetration, the coating became too delicate to protect the yarn from abrasion. If the concentration was increased the final result was a heavy sticky coating. Tests have indicated that a No. 12 grade of gelatin was likely to be best for the slashing of acetate yarns. Cuprammonium and viscose are highly water absorbent and offer little resistance to penetration by the size. A No. 9 gelatin grade is usually most satisfactory for the size solutions. Gelatin standards for the different deniers have been suggested. For crepe soaking:

Higher crepe soaking	No. 18
Regular crepe soaking	No. 15

For slashing viscose and cuprammonium:

Slashing finer deniers	No. 11
Slashing medium deniers	No. 10
Slashing coarse deniers	No. 9

Numbers 11 and 12 are the grades recommended for slashing acetate, with the No. 12 for the finer deniers.

In materials made of two different yarns, two slashing and scouring operations are required, which can be eliminated in the case of a cotton and rayon mixture if the sizes are prepared separately. The starch solution should be cooled to 150 to 160°F., and then the gelatin added. The latter aids in the removal of the starch in the desizing operation in a period of about 15 minutes at a temperature of 180 to 190°F.

Overcooking of the sizing is to be avoided, because if it becomes carmelized, it cannot be removed from the gray goods without the use of powerful detergents which may damage the yarn.

Foaming of the sizing solution is largely the result of mechanical causes and from the pH of the softening agent used. Tests indicate that the best results can be obtained by using softening oils with a pH well above 6.2. Foaming also occurs if the gelatin is not soaked in cold water prior to dissolving it in hot water. For best results the gelatin should be stirred into cold water for at least 15 minutes, and then melted at 140°F.

Size spots or "tear drops" in slashing of rayon warps refer to spots where adjoining threads of the warp are bonded together by the size. These spots are caused by very fine particles of undissolved gelatin which are present in the suspension in the size pan of the slasher. As the squeeze rolls revolve, the gum-like particles are picked up and squeezed on the warp, and when they pass through the split bars, the adjacent warp ends are ripped apart causing a defect in the woven fabric. To prevent this, the completed size should be strained through a clean layer of cloth resting upon a fine wire filter for the retention of occasional undissolved particles.

The properties of gelatin grades established by the National Association of Glue Manufacturers, Inc., are shown in Table 34.

Table 34. Properties of Gelatin Grades[1]

Association Grade Number	Jelly Strength (g.) Grade Range	Viscosity (mp) Grade Range
8	178-206	65-72
9	207-236	73-80
10	237-266	81-89
11	267-298	90-98
12	299-330	99-108
13	331-362	109-118
14	363-394	120-130
15	395-427	131-142
16	428-460	143-155
17	461-494	156-168
18	495-526	170-185

[1] H. B. Sweatt, Director of Animal Glue Information Service, National Association of Glue Manufacturers, Inc., *Textile World*, **96**, No. 3, 141 (1946).

European practice in sizing and finishing of textiles with specific relation to the hydrophilic gums has been reviewed by de Keghel.[8]

Mukoseev[9] states that "A textile size, equal or superior to the usual starch size, was made by replacing half of a 90-kg. batch of rye flour (in 700 liters of water) by 24 kg. arabic, heating nearly to boiling, adding 4 liters of a solution of castor oil 16.5, oleic acid 2.5, 20° Bé. sodium hydroxide 7.5 in water 23.5 kg., and further adding 1 liter of oleic acid, boiling 20 minutes and neutralizing with acetic acid."

Henk[10] described the Continental application of gelatin in textile finishing as a protective colloid in boiling out cotton, as a dispersing agent for lime soap, as a stabilizer for oleic acid emulsifying agents, and a dyeing assistant, as a reserve for indigosol dyeing and printing, as a sizing medium, and for the protection of wool during chlorination in anti-shrink processing.

Colomb[11] gives a series of practical formulae for the application of gelatin and glue in dyeing and finishing in French practice, with particular reference to silk and rayon.

Ranachandran and Venkataraman[12] suggested as a result of their study that the water extract from the husk powder of psyllium seed, after decolorization and purification from extraneous matter, is useful in printing and finishing. They discuss Indian practice when the material is mixed with starch paste and with additions such as commonly employed for sizing materials of yarn. The psyllium seed extract, however, cannot be employed in vat printing as a result of its sensitivity to alkalies.

Colomb[13] has described the possible uses of the alginates in textile finishes with a series of specific formulations which were the subject of experimentation.

Gruart[14] claims the use of alginates for stiffening fibrous materials, as mordants in dyeing of cotton and wool, as emulsifying and dispersing agents for various materials to be applied to textiles, and suggests the application of aluminum alginate for waterproofing fabrics.

Frieden[15] suggests the adhesive joining of gelatin-coated surfaces by treating one of the gelatin coatings with an aqueous solution of a trivalent

[8] M. de Keghel, *Tiba*, 4, 517-23, 657-63, 933-7, 1199-1207, 1457-63 (1926); 5, 161-9, 319-23 (1927).

[9] N. A. Mukoseev, *Tekstil. Prom.*, No. 1/2, 23-4 (1943).

[10] H. J. Henk, *Gelatine, Leim, Klebstoffe*, 10, 127-9 (1942); *Chem. Zentr.*, I, 1836 (1943).

[11] P. Colomb, *Teintex*, 2, 328-40 (1937).

[12] S. R. Ranachandran and K. Venkataraman, *J. Soc. Dyers Colourists*, 54, 462-4 (1938).

[13] P. Colomb, *Teintex*, 3, 94-101 (1938).

[14] A. H. Gruart, British Patent 456,342 (Nov. 3, 1936) (See French Patent 789,392, Oct. 31, 1935).

[15] A. Frieden (assignor to American Sealcone Corp.), U. S. Patent 1,927,166 (Sept. 19, 1933).

metal salt and an alkali such as aluminum sulfate and sodium hydroxide to give a pH of 3.5 to 5.2.

Many of the waterproofing or showerproofing treatments applied to textiles are dispersions of wax-like materials in water with emulsifying oils or compounds. The hydrophilic gums are usually present in small quantities as "protective agents" to maintain the stability of the emulsion. Beeswax, carnauba wax, various paraffin waxes, are commonly employed with aluminum salts to form aluminum soaps with the tree exudation gums or seaweed colloids as stabilizers or protective agents.

Powder colloidal preparations[16] have been suggested. These are to be made by atomizing and drying a colloidal emulsion containing a lipoid-sol, a lyophobe substance, and a protective colloid. Typical would be a colloidal paraffin emulsion containing 20 per cent paraffin, 4.5 per cent gelatin or hydrophilic colloid, 2 per cent boric acid, 10 per cent aluminum sulfate, and 63.5 per cent water. This material is atomized and dried. The powder may be redispersed and used as an impregnating bath for "water-proofing."

Wale[17] has suggested a fabric reinforcement by coating or impregnating with a plastic cement composed of silicates of sodium, ferric oxide, soap, soda, carnauba wax and arabic. The coated fabric may serve as a filling between the insole and outsole of boots and shoes, etc.

Chandler[18] suggested improved sizing materials containing ammonium thiocyanate and arabic for cellulose acetates.

Textile Printing

Textile color designs and patterns are obtained either by weaving or knitting colored yarns or by printing. Printing is in many ways more versatile, faster, and more economical. The woven cloth, desized, bleached (also frequently mercerized or dyed) and dried is printed upon by any of a number of methods. Most of the methods, including the most important one, roller or machine printing, require color pastes. The color pastes consist of a thickening, water, a dye, mordants, dyeing assistants, a hygroscopic substance, and other chemicals.

After the design is printed, the fabric is dried for ease of handling. The printed color must be fixed. Generally on cotton the color is set by "ageing" which consists in steaming for 1 to 10 minutes at 190° to 212°F. or by "steaming" which consists in steaming for ½ to 2 hours at 215° to 220°F. In both cases, there should be sufficient moisture present to soften the dried paste and permit the dye to penetrate into the cloth and react

[16] *Soc. pour L'ind. chim. à Bâle,* Swiss Patent 168,722 (July 16, 1934), (Cl. 36*e*).
[17] W. H. Wale, British Patent 433,207 (Aug. 8, 1935).
[18] C. F. Chandler, (assignor to Du Pont Rayon Co.,) U. S. Patent 1,943,000 (Jan. 9, 1934).

with the chemicals present in the printing paste to color the cloth to a high degree of fastness. At the same time there should not be so much water present as to cause a running of the paste. Chrome, basic and direct colors are steamed; vats, soluble vats and insoluble azo colors are aged.

Much of the behavior during application and the characteristics of the final printed cloth depend upon the thickening employed. They are generally made up in advance and kept as stock pastes, being drawn upon to make up the different printing pastes as required. Each plant keeps several types of pastes on hand.

Formulation of the printing color paste must fulfill requirements of a range of viscosities, body, and other characteristics. This requires skill in selection of the ingredients and in the formulation. The printing paste must fill the engravings of the design rollers and permit the rapid removal of excess by the doctor blade or knife. The paste must be pressed into the cloth, yet remain within the limits of the desired pattern or design and it must permit the color to be fixed. The ability of a printing paste to give a fine line, a delicate design, lightly engraved blotches, heavy blotches, a blending of colors, a sharp definition of colors, penetration of color to the back of the cloth, and a great many other appearances is in a large measure dependent upon the thickening used. The condition of the engraving, the type of fabric construction, and the dyestuff also play an important part in the character of the print and affect the selection of the thickening used. The thickening primarily insures uniform distribution of the dyestuff and other ingredients and imparts the necessary viscosity and body. It must meet many other specific requirements as well.

After fixing the color the thickening agent may be either washed out from the fabric and the printed pattern or it may be permitted to remain. In the latter case, the thickening may be one so selected that it may become an integral part of the fixed color. It may be desired that the thickening agent remain on the fabric to avoid washing to save the cost of this operation or because the colors are cheap and would wash out. The handle of the cloth after the thickening agent is washed out is dependent too upon the character of that agent and the degree of its removal. Where the thickening agent is left in the cloth, it obviously also affects the handle.

Thickeners fall into two broad groups. In one group are those used solely as thickening agents and later removed as completely as possible from the fabric. Their function is to act as a vehicle for carrying the color to the cloth and to prevent the spread of color by capillarity beyond the desired areas, yet they should not have an affinity for the colors or mordants with which they are mixed, otherwise on being washed out of the fabric they will carry out much of the color. Arabic, Senegal, traga-

canth, karaya, and locust bean, starch, flour, dextrin, British gum, and sodium alginate are in this group. China clay and related materials are frequently employed along with these. The other group acts both as thickening agents and also as fixing agents, remaining on the cloth as an integral part of the finished color. In this group are albumen and casein, which are both coagulated by heat. By steaming they change to an insoluble form and fix the dye on the fiber. Casein does not work as well as albumen generally, but is cheaper.

The thickenings are made up as stock pastes in advance and kept on hand to be mixed with dye pastes, chemicals and water to give the printing pastes desired. For cotton, the most common thickeners are starches, British gum, and the neutral gums. Irish moss, sodium alginate, some synthetic gums and many specially prepared printing gums are also commercially available. Some of the typical thickenings which contain gums are given below:

ARABIC THICKENING
(*Starch Reduction Paste*)

Gum arabic	50 lb.
Water	50 lb.
Total	100 lb.

Mixing directions:—Soak in cold water for several hours, boil to smooth consistency, strain, store, allow to settle, and decant.

Arabic is particularly suited for printing paste blotches or backgrounds. It washes out very well and it leaves a soft feel. It finds use in printing soft goods, flannelettes, sateens and other materials where the cost will allow, especially if the pattern contains heavy masses of solid color.

ALKALINE BRITISH GUM-VEGETABLE GUM THICKENING[19]
(*Starch Reduction Paste*)

British gum	40 lb.
Potassium carbonate	16 lb.
Water	20 lb.
Glycerol	10 lb.
50% arabic (or 6% tragacanth, or 3% locust bean)	14 lb.
Total	100 lb.

Mixing directions:—Dissolve the potassium carbonate in water, add the British gum and heat until dissolved, add the glycerol and vegetable gum solution. Cool and strain.

[19] G. R. Merrill, A. R. Macormac, and H. R. Mauersberger, American Cotton Handbook, American Cotton Handbook Company, New York, 1941.

KARAYA THICKENING (20%)[20]

Karaya (finely ground)	200 kilos
Sodium peroxide	1.25 kilos
Hydrochloric acid (30°Tw)	see below
Water	sufficient
	1000 liters

Mixing directions:—The karaya is mixed well with 500 kilos of water, then 0.6 kilos of sodium peroxide in 125 kilos of water is gradually added with stirring for 1 hr., then add 0.65 kilos of sodium peroxide in 75 kilos of water, stir ¼ hr., bring to a boil, boil for 3½ hr., neutralize with the hydrochloric acid and make up to 1000 liters.

Karaya thickening is also made by boiling under pressure in an autoclave. When so made, there is no need to grind the gum nor to add any sodium peroxide and the solution takes place more rapidly. The product made in the autoclave is, however, darker and for many colors must first be bleached with oxidizing agents such as hypochlorites or peroxides.

Karaya thickenings often find use as a substitute for arabic. The printing of blotches, discharges, reserves, and flannelettes is the principal use.

GUM THICKENING[21]

Karaya	33 lb.
Water	67 lb.
Total	100 lb.

Mixing directions:—Soak the gum in the water, boil for 2 to 2½ hr. under about 2 atm. pressure.

These thickenings are generally slightly dark in color. They are inexpensive and suitable for resist printing colors particularly with vat and immedial dyestuffs. The above thickener is also dried and sold as such. To be used, one need only add 2 parts of water to 1 of the dried gum.

TRAGACANTH THICKENING (60:1000)[22]

Tragacanth	6 lb.
Water	94 lb.
Total	100 lb.

Mixing directions:—Soak the tragacanth 24 hr. with the water and boil with stirring for 8 to 10 hr.

This thickening is easily washed out from the fiber and is used in yarn printing and in printing very fine fabrics where an extended and vigorous

[20] E. Knecht and J. B. Fothergill, "The Principles and Practice of Textile Printing," Charles Griffin & Co. Ltd., London, 1936.

[21] "Manual for Printing Cotton and Other Fibers of Vegetable Origin," No. 975, General Dyestuff Corp., New York, 1937.

[22] "Manual for Printing Cotton and Other Fibers of Vegetable Origin," No. 975, General Dyestuff Corp., New York, 1937.

washing would impair the desired soft handle of fine goods. It is also used where goods are not rinsed, yet must have a soft handle. This thickener also is used for thickening padding liquors, especially in conjunction with wheat starch pastes.

NEUTRAL STARCH–TRAGACANTH THICKENING[23]

Wheat starch	7-15 lb.
Tragacanth thickener (60:1000)	25 lb.
Olive oil	3 lb.
Water	sufficient
Total	100 lb.

Mixing directions:—The wheat starch is made into a paste with 7 to 15 lb. of water and the tragacanth thickener, olive oil and 42 to 58 lb. of water are stirred in and the whole boiled.

This thickener is said to level well and is used in steam colors for pale to dark shades. It is suited for printing with indigosol, vat dyestuffs and for oxidation discharges. Minus the olive oil, it is also suitable for Rapid Fast, Rapidogen and Rapidazol dyestuffs and for base and naphtholate printing.

ACETIC ACID STARCH–TRAGACANTH THICKENING[24]

Wheat starch	10-15 lb.
Tragacanth thickening (60:1000)	25 lb.
Olive oil	3 lb.
30% acetic acid (9°Tw)	10-12 lb.
Water	sufficient
Total	100 lb.

Mixing directions:—The wheat starch is pasted up with 10 to 15 lb. of water, then the tragacanth thickener, olive oil, and 30 to 42 lb. of water are stirred in and boiled up, after which the acetic acid is stirred into the hot paste.

This thickening is frequently used for steam colors (basic and mordant dyestuffs). It is particularly suitable for dark and medium shades.

ACETIC ACID FLOUR–TRAGACANTH THICKENING[25]

Wheat flour	21 lb.
Tragacanth thickener (60:1000)	30 lb.
30% acetic acid (9°Tw)	4 lb.
Water	45 lb.
Total	100 lb.

Mixing directions:—The wheat flour is pasted up with the water, then stirred with tragacanth thickening and the acetic acid added and the whole boiled up.

[23] "Manual for Printing Cotton and Other Fibers of Vegetable Origin," No. 975, General Dyestuff Corp., New York, 1937.

[24] "Manual for Printing Cotton and Other Fibers of Vegetable Origin," No. 975, General Dyestuff Corp., New York, 1937.

[25] "Manual for Printing Cotton and Other Fibers of Vegetable Origin," No. 975, General Dyestuff Corp., New York, 1937.

This thickening is suited for printing diazotized bases.

LOCUST BEAN THICKENING[26]

(*Starch Reduction Paste*)

Powdered locust bean	3 lb.
Cold water	97 lb.
Total	100 lb.

Mixing directions:—Stir gum into the water thoroughly. Allow to swell overnight. Boil up with constant stirring, cool and strain. Phenol (0.1 per cent) serves as a preservative.

Basic dyestuffs and some mordant dyestuffs are precipitated by locust bean gum.

ACID FLOUR–LOCUST BEAN GUM THICKENING[27]

(*Starch Reduction Paste*)

Wheat flour	20 lb.
Water	45 lb.
Glacial acetic acid	5 lb.
3% locust bean thickening	30 lb.
Total	100 lb.

Mixing directions:—Mix flour and water together thoroughly, add locust bean thickening, heat mixture to a smooth paste with constant stirring while adding the acetic acid.

CARRAGEEN THICKENING[28]

Carrageen moss	5-10 lb.
Water	95-90 lb.
Total	100 lb.

Mixing directions:—Allow the moss to swell in the water for 24 hr., then boil and stir while cooling.

KELTEX (SODIUM ALGINATE) THICKENING

Keltex	2.5-4.0 oz.
Water	1 gal.

Mixing directions:—Keltex is added with rapid agitation to the whole amount of water within 2 to 3 minutes so that the solution will not have time to thicken before all the sodium alginate has been added. Complete solution usually requires from 15 minutes to an hour or more depending upon the degree of agitation. The use of 4.0 oz. per gal. gives an extremely heavy paste.

Keltex is compatible with starch, dextrin, British gum, karaya or prepared textile gum pastes. Keltex paste contains approximately 0.1 per

[26] G. R. Merrill, A. R. Macormac, and H. R. Mauersberger, American Cotton Handbook, American Cotton Handbook Company, New York, 1941.

[27] G. R. Merrill, A. R. Macormac, and H. R. Mauersberger, American Cotton Handbook, American Cotton Handbook Company, New York, 1941.

[28] "Handbook of Printing," 1st English Ed., Chemical Works, (formerly Sandoz), Basle, Switzerland, 1937.

cent of a preservative, Dowicide B. Plain Keltex has no preservative and the paste must be protected against spoilage if kept.

Keltex paste is said to be suited for use with direct dyes on rayon in machine and screen application; Rapidogen or Indigosol dyes on cotton or rayon in machine but not screen printing, usually used in conjunction with a starch paste; vat dyes on cotton; discharge pastes on cotton or rayon; and acetyl or Celliton colors on celanese. It cannot be used with chrome dyes, basic colors or naphthol salt colors.

The formulation and technique of application of printing pastes has been practically entirely developed by the method of trial and error and even today the control of consistency and other behavior of the pastes is gauged by personal judgment and trial and error.

Glarum[29] in a fundamental study on vat printing pastes showed correlations of physical properties, especially flow characteristics, and printing quality. Good printing was generally obtained with vat printing pastes whose fluidity (i.e., revolutions per second obtained with a Stormer viscosimeter divided by the load in grams) was low over a wide range of loads, while the poorest printing was obtained when fluidities were high over a large part of the load range. The fluidity-load ranges of good, fair, and poor printing pastes were fairly well defined so that evaluation of printing quality may be measured by this means. Few if any plants, however, use this as a control method.

The Rhode Island section of the American Association of Textile Chemists and Colorists[30] studied the factors affecting color yield in vat color printing with particular attention to the effect of thickeners including British gums, gum tragacanth, and karaya. They concluded that an ideal paste for vat color printing should prevent the re-agglomeration of color particles; it should have no protective colloid action which retards the fixation of color on the fiber. In addition, the vat color paste should have the proper cohesion so that it maintains this body and adhesion when it is printed on the cloth. The paste should give minimum penetration and therefore maximum dyestuffs yield. When tragacanth was used as a paste it caused re-agglomeration of color particles, but the color printed with it did not wash off in development and soaping. Penetration was greater with tragacanth than with a starch British gum paste employed as a standard. Karaya paste also caused re-agglomeration, but gave increased penetration to the fabric so that lower color yields were obtained.

[29] S. N. Glarum, *Am. Dyestuff Reptr.*, **23**, 175 (1934); **25**, 150 (1936); **26**, 124, 437 (1937).

[30] *Am. Dyestuff Reptr.*, 509-9 (Dec. 4, 1944).

Chapter 14

Miscellaneous Applications

The use of gelatin as a food in many different forms is too well known to warrant discussion here. It forms the base of many confectionery items and all of the gums have been employed in this field to a greater or lesser extent. Agar, the alginic acids, and the alginates have been rather widely suggested as bulk materials in low-nourishment content food for diabetic and obese persons. Seaweed, Irish moss, Iceland moss and the like are often employed in foods of low-nutrient value in many different countries of the world.

In a number of applications, the seaweed colloids have been suggested as competitive materials to gelatin. Typical is the suggestion of surface-sizing of paper with agar or Irish moss.[1] Agar and carrageen are odorless, tasteless, free from nitrogen and their gelatinous property is greater than that of gelatin as a surface-sizing material for paper. The dry moss, washed with water, is immersed in 50 parts of water and heated for an hour on the water bath. After filtering the solution through a cloth, a weight of sugar equal to the moss is added and the solution evaporated to a jelly. Salicylic acid or boric acid may be added as a preservative. After drying, the product is insoluble in cold water but soluble in hot.

Altman[2] employed agar and sugar with boric acid. A sizing mixture is prepared by heating 1 part of agar pulverized to powder, with 45 to 50 parts of water for 1 hr. on a water bath. The solution is strained through cloth, 1 part sugar added, the liquor concentrated to jelly, stabilized by addition of boric acid or salicylic acid, and bleached by passage of ozone through it. The jelly is soluble in hot water. One kg. of pulp requires 50 g. agar, 50 g. sugar, 850 g. water, and 50 g. talc.

Hayward[3] treated paper with gum arabic-containing compounds. A formed and dried web is treated on both sides with a filler in colloidal suspension such as an aqueous mixture containing arabic, glycerol, and pigment, and the web is passed between non-yielding pressure rollers by which the filler material is forced into the interstices between the fibers.

[1] Anon., *Wochbl. Papierfabr.*, 57, 1186-7 (1926).
[2] P. E. Altman, *Chem.-Ztg.*, 48, 777 (1924).
[3] R. A. Hayward, (assignor to Kalamazoo Vegetable Parchment Co.), U. S. Patent 1,987,901 (Jan. 15, 1935).

Starch-treated paper[4] has been made with auxiliary agents such as the gums. Paper is treated on either one or on both sides with uncooked starch made into a slurry with water, with or without a pigment, and the adhesive properties of the starch are developed on the paper by heating. Various other auxiliary substances also may be used such as arabic, waxes, dyes and other coloring substances, and softening agents such as glycerol or castor oil.

Decorative papers[5] employ the gums and dextrins as adhesives. Aluminum flakes or other coloring substances are used with a carrier or vehicle such as dextrin, glucose, sucrose, or arabic and sprinkled onto the pulp layer while it is in the wire of the paper machine. British patent 239,880 specifies the use on the pulp layer of aluminum flakes or granular aluminum.

The application of British gum and dextrin as adhesive on envelopes, stamps, and the like, is well known and has been discussed under dextrin. British gum is sometimes recommended as a coating[6] over other transparent coatings. Paper which is transparent, tough and capable of being stamped is made by coating pure cellulose paper free from lignified fibers with a mixture of digested wheat starch, castor oil, glycerol, and coloring matter and drying. The reverse side may also be coated. The coatings are then covered with a glaze, such as dextrin, and cold-glazed. The paper is used for making artificial flowers and foliage. In this particular field locust bean gum is a competitor because of its difference in properties.

The hydrophilic gums have been employed as stabilizing or protective colloids in wax emulsions for the preparation of waxed or coated papers, or in the printing masses used for wallpaper decorations or sizing after decoration. Kelp and the alginates have been proposed as a binder for asbestos in paper making.[7] MacLaurin[8] patented an ornamental paper in which paper is coated with a solution of mannitol, allowed to dry and the drying is controlled by a hydroscopic agent such as glycerol and tragacanth in the solution so that the greater part of the coating will be converted into flake-like crystals.

Cate[9] described the alginates as primary coatings for paper for food containers. For a primary coating, an aqueous solution of substantially 1 per cent of a water-soluble alginate such as that of sodium having a Woolwich viscosity of about 2 sec. is employed; and, after drying, a solution of a water-soluble alginate having a Woolwich viscosity of about 50

[4] Champion Coated Paper Co., British Patent 333,226 (July 15, 1929).
[5] A. C. Dodman, British Patent 239,879 (Sept. 13, 1924).
[6] J. Hoffman, German Patent 592,524 (Feb. 8, 1934).
[7] A. L. Kennedy (assignor to Plastic, Inc.,) U. S. Patent 1,830,607 (Nov. 3, 1932).
[8] J. MacLaurin, U. S. Patent 1,724,672 (Aug. 13, 1929).
[9] P. H. Cate (assignor to Kelco Co.,) U. S. Patent 2,290,686 (July 21, 1943).

sec. renders the paper resistant to waxes, oils, and organic solvents; the second coating is dried, and an outer coating is applied which is formed from a solution of wax or a resin.

Many gummed papers have been proposed consisting of layers of the natural gums, or of gelatin and the gums or of hydrophilic colloids and the gums in a wide range of compositions.

In general, the hydrophilic colloids with the exception of British gum do not compete with the much cheaper starch suspension of rosin or resin nature sizes for paper of the tonnage varieties. The gums are employed only in special papers, constituting only a small percentage of the entire paper output.

The alginate esters of amines such as triethanolamine and ethanolamine have been proposed as coating materials which are resistant to mold.[10] By reaction of triethanolamine and alginic acid, a product is obtained which is resistant to molds and microorganisms producing liquefaction and decay and which is suitable for coating cheese, meat and other food products, glass, metals, wood, plastics, ceramic ware and plaster (suitably with various admixtures such as sucrose, dextrin, starch, glucose, fructose, maltose, xylose, glycerol, treated gelatin or glue, ethylene glycol, propylene glycol, basic compounds of sodium, ammonium, aluminum, zinc, potassium, etc., or a compound such as sodium orthophosphate (Na_3PO_4, Na_2HPO_4), ammonium phosphate or sodium carbonate serving as a stabilizer when the product is used with water containing calcium compounds in solution). U. S. Patent 2,158,486 related to mixed alginic acid salts of inorganic substances and ethanolamine of the formula $A(x)_n\ (y)_n$ where A is the radical of alginic acid, x is from the group which consists of the alkali metals, the alkaline earth metals, zinc, aluminum and copper, y is ethanolamine, and n is a whole number consistent with the basicity of the acid and the remaining substances. A process of preparing mixed ammonium triethanolamine-alginate consists in mixing approximately 1000 lb. of wet alginic acid containing 10 per cent alginic acid solids, approximately 70 lb. of triethanolamine-alginate, and 10 lb. of approximately 26° Bé. aqua ammonia. A process of manufacture of mixed ethanolamine salts of alginic acid and metals comprises mixing moist alginic acid, ethanolamine and a hydroxide of an alkali metal, alkaline earth metal, zinc, aluminum or copper, in stoichiometric proportion, and agitating the mixture until chemical combination occurs. U. S. Patent 2,158,487 also relates to the production of triethanolamine alginate (as by mixing the reactants into a pasty product) and of a propanolamine or butanolamine salt of alginic acid.

Alginates have been suggested as additives to food and beverages con-

[10] B. Preble (assignor to Kelco Co.,) U. S. Patent 2,158,485 (May 16, 1939).

taining milk or cream[11] and evaporated milk[12] or as food products,[13, 14] as well as in tablet form.[15]

Films have been prepared from the alginates[16] by mechanical processes.

The use of bottle caps and formed articles of gelatin stabilized with formaldehyde has been well known. Artus[17] described the procedure of proper adjustment of hardening agent and plasticizer. Much improvement is possible in producing from gelatin such articles as bottle caps and formed items. Formaldehyde is the usual hardening agent. One hundred parts of dry gelatin will take up 4.8 parts ordinary formalin solution. Gaseous formaldehyde will be taken up more slowly but to the same total amount. The reaction is reversible and the formaldehyde-hardened gelatin can again be made soluble by repeated treatment with hot water, with 15 per cent hydrochloric acid or with ammonium hydroxide. Gelatin can also be hardened by treatment with sodium hypochlorite, 10 g. gelatin taking up 9 per cent chlorine in 20 minutes from a solution containing 100 g. sodium hypochlorite and 2 g. hydrochloric acid in 400 g. water. The plasticizers and their relative properties are not discussed.

Bauer, Bauer and Hawley[18] suggested an amylaceous, water-soluble adhesive such as a dried composition containing British gum and glycerol be moistened with a solution containing borax and urea (various similar compositions and treatments also being described).

Fischer[19] recommended the treatment of seeds before planting with protective colloidal material such as gelatin, agar, or similar products. Seeds such as alfalfa, clover, beans, etc., are coated with a protective colloidal material such as gelatin, or agar, which is dried, and with overlying coatings of plant food and insecticidal materials, inoculating bacteria, etc.

Roure[20] proposed indelible ink made by dissolving salicylic acid 2, arabic 25, alum 100 and oxalic acid 50 g. in 1 liter of water, boiling and adding 100 cc. of alcohol to make solution A. Aniline dyes according to the color of ink desired are added to a boiling solution of 20 cc. of hydrochloric acid in 1 liter of water to form solution B. Solutions A and B are mixed, allowed to stand and then filtered. Neumann[21] used gelatin coat-

[11] H. J. Lucas (assignor to Kelco Co.), Canadian Patent 406,239, (July 21, 1942).
[12] V. K. Wilt (assignor to Kelco Co.), U. S. Patent 2,223,277, (Nov. 26, 1941).
[13] P. R. Park (assignor to Philip R. Park, Inc.), U. S. Patent 1,983,595 (Nov. 27, 1935).
[14] P. R. Park (assignor to Philip R. Park, Inc.,) U. S. Patent 1,875,352 (Sept. 6, 1933).
[15] M. J. Walsh, *Food Industries*, 5, 229 (1933).
[16] C. W. Bonniksen, British Patent 492,264 (Sept. 13, 1938).
[17] F. v. Artus, *Gelatine, Leim, Klebstoffe*, 6, 75-7 (1938).
[18] H. F. Bauer, J. V. Bauer and D. M. Hawley (assignors to Stein, Hall Mfg. Co.), U. S. Patent 2,167,629 (Aug. 1, 1939).
[19] A. C. Fischer, U. S. Patent 2,168,332 (Aug. 8, 1939).
[20] M. Roure, French Patent 692,929 (June 28, 1929).
[21] H. Neumann, U. S. Patent 1,989,017 (Jan. 22, 1935).

ings in collotype printing. For obtaining gelatin coatings of even thickness, a thin sheet of material such as paper is first thinly coated with an aqueous solution such as one of starch and sugar, allowed to dry, then coated with a molten gelatin composition, which after setting is transferred to a zinc plate or the like.

Lindstaedt[22] formed addition compounds between alkaloids and gums. An alkaloidal material containing a pyridine ring, such as nicotine, coniine, bipiperidyl and their compounds and salts is caused to react with a gum or resin, such as tragacanth, agar, Indian gum or shellac (preferably using an excess of the gum or resin if the product is to be administered to animals as a parasiticide).

It is stated that the water resistance of dextrin pastes[23] is increased by mixing a finely divided vegetable protein, e.g., glutin, with the dextrin. The paste is then made by adding water and cooking. The protein may be added as a mixture of cornstarch and corn glutin that has been gelatinized by passage between heated rolls.

Similarly it is held that adhesives[24] such as glue, gelatin or gum are improved by adding alcohols of high molecular weight or sulfonation products thereof, such as lauric alcohol, or a sulfonate of cetyl or oleyl alcohol.

The gums are considered as binders in various patented crayons for writing on sand-blasted glass.[25]

Eckrich and Eckrich[26] described a dip or coating for meats or other food products. A product for coating meats comprises gelatin and water in the approximate proportion of 1 to 3 and a fatty material such as coconut oil or lard, which will solidify at atmospheric temperature, homogeneously mixed to give a consistency approximately that of the white of a hard-boiled egg (the proportion of the gelatin solution to fatty material being about 4 to 3). The product is suitable for coating liver sausage, liver loaf and other meat loaves and meat products.

Grettie[27] held that a bleached and deaminized gelatin shows improved whipping qualities in the manufacture of marshmallows. Collins[28] eliminated objectionable caking and quickened the setting of gelatin, sugar and flavoring compounds in gelatin desserts by addition of sodium bi-

[22] F. F. Lindstaedt, (assignor to Hercules Glue Co., Ltd.), U. S. Patent 2,065,190 (Dec. 22, 1937).
[23] International Development Co., British Patent 453,132 (Sept. 4, 1936).
[24] Deutsche Hydrierwerke A.-G., French Patent 762,881 (Apr. 19, 1934).
[25] C. W. Hart, U. S. Patent 2,226,377 (Dec. 24, 1941).
[26] H. C. Eckrich and H. J. Eckrich, Sr. (assignors to Peter Eckrich & Sons, Inc.), U. S. Patent 2,161,029 (June 6, 1939).
[27] D. P. Grettie (assignor to Industrial Patents Corp.), U. S. Patent 2,158,117 (May 16, 1939).
[28] W. R. Collins (assignor to Standard Brands Inc.), U. S. Patent 2,196,146 (Apr. 2, 1940).

tartrate, lactate, acetate or citrate to yield a water solution having a pH of 3.0 to 4.7. Grettie[29] states that addition of 0.5 to 5 per cent of sodium hexametaphosphate improves the whipping quality of gelatin for marshmallows without affecting its viscosity or jelling strength.

Esmond and Duecker[30] proposed non-blooming chocolate coatings by the addition of gelatin and processing in a specific manner.

A medicinal food was suggested by Hickey[31] in that raisins or other dried fruits are coated with medicinal substances, e.g., mucilage of acacia, phenolphthalein, citric acid, extract of senna and aromatic extract of cascara sagrada. Musher[32] described the production of an expanded, structure-disrupted, medicinal, low-starch bulk-producing and mucilaginous exuding seed, the interior of which was expanded to a greater volume than in its original condition. The interior was rendered relatively porous and relatively more water absorbent. The expanded seed substantially retained its unity and is suitable for use in mixtures with various other food or medicinal materials.

Leo, Taylor and Lindsey[33] stated that gum solutions in beverages have a tendency to precipitate pectin in that they contain the enzyme pectinase. When gum solutions, such as a 20 to 40 per cent solution of arabic, are heated at pH 5.0 for 15 minutes at 200°F. and then for 1 hr. at 170 to 200°F., the troublesome enzymes are destroyed and the precipitation of the pectin is prevented.

Johnstone[34] states that insoluble flavor oils are usually suspended in the water phase by means of arabic, other emulsifying agents generally being unfit in one way or another. The finely powdered gum is added to the oil; this is then added to the water and the whole forced through a conical needle-valve with a clearance of a few thousandths of an inch at pressures of 2500 to 5000 lb. per sq. in.

Bullard[35] suggested health biscuits made by dissolving agar in boiling water and the solution mixed with a coarse ground wheat 10, barley 2, oats 1, and agar 0.5 parts. The mixture is dried in an oven, ground into meal, sweetened with sugar or honey, shaped and baked.

Agar desserts are suggested by Allnut[36] similar to those of gelatin, water and flavoring substances such as fruit juices, fruit acids and sugar.

[29] D. P. Grettie, U. S. Patent 2,196,300 (Apr. 9, 1942).
[30] L. B. Esmond and W. W. Duecker (assignors to Essex Gelatin Co.), U. S. Patent 1,894,677 (Jan. 17, 1933).
[31] C. M. Hickey, U. S. Patent 1,598,348 (Aug. 31, 1926).
[32] A. Musher, (assignor to Food Mfg. Corp.), U. S. Patent 2,278,464 (Apr. 7, 1942).
[33] H. T. Leo, C. C. Taylor and J. W. Lindsey (assignors to Mutual Citrus Products Co.), U. S. Patent 2,380,115 (July 10, 1945).
[34] C. Johnstone, *Mfg. Confectioner*, 19, No. 4, 14-16 (1939).
[35] A. Bullard, British Patent 398,360 (Sept. 14, 1933).
[36] R. J. Allnut, (assignor to Homfreeze Corp.), British Patent 302,883 (Dec. 23, 1927).

Cartier and Gloess[37] hold that marine algae are made palatable by treatment with bases such as magnesia which form soluble compounds with the colloidal matter therein.

Irish moss can be substituted for agar as a jelling agent in canned precooked chicken.[38] Gelose, obtained from the moss by extraction in hot water, is undesirable in color and taste, but treatment with activated charcoal and filtration through diatomaceous earth removes all odor and taste and most of the color. Gel strength is somewhat less with Irish moss than with agar for the same amount of jelling agent added, but the presence of small amounts of potassium salts brings up the strength of the moss jellies to that of the equivalent agar jellies.

Tuvin[39] recommended psyllium seeds for use as a food accessory. Psyllium seeds are coated with sugar and then with an overlying coating of a moisture-absorbing gum such as India gum.

Rezos[40] preserved berries, grapes, cherries or similar foods when washed in a dilute tragacanth solution, packed with a relatively small proportion of sugar and frozen.

Tragacanth is held to be a good mechanism for the preserving of food.[41] Food is covered with a gum such as tragacanth capable of swelling in the presence of water without becoming sticky. Antiseptics or preservatives such as an alkali nitrate or bisulfite are then added to the gum.

Buchanan[42] stated that a compound useful in the confectionery and bakery industries which could be readily dispersed in water without lumping is manufactured by the dispersion of gums such as ammonium or sodium alginate or tragacanth whose dispersion is facilitated by the presence of soluble salts of lactic acid in the proportion of 0.3 to 2.5 per cent by weight of the lactate and moistened with 0.2 to 5 per cent of water.

[37] A. Cartier and P. Gloess, French Patent 633,696 (Sept. 8, 1926).
[38] *Oil, Paint Drug Reptr.*, 20, (Apr. 17, 1944).
[39] L. A. Tuvin, U. S. Patent 1,891,697; 1,891,698 (Dec. 20, 1933).
[40] M. Rezos, U. S. Patent 1,582,858 (Apr. 27, 1926).
[41] Stabavite Syndicate, Ltd., French Patent 655,688 (June 13, 1928).
[42] B. F. Buchanan (assignor to American Maize-Products Co.), U. S. Patent 2,376,656 (May 22, 1945).

Chapter 15

Specifications, Identification, and Testing

Specifications for the various gums, with identification tests have been more thoroughly worked out in connection with medicine and pharmacy than any other field. Some of the more extensive descriptions are found in the various editions of the U. S. Pharmacopoeia, the corresponding British references, and the various formularies. Typical drug evaluations are given on the pages following for acacia or arabic, agar, chondrus or Irish moss, gelatin, linseed or flaxseed, and tragacanth.

Specifications of the Gums

Acacia—Gum arabic[1]

Description and physical properties.

Unground acacia:

Form.—Appears as spheroidal tears up to 32 mm. in diameter or in angular fragments.

Color.—Yellowish-white to light amber and translucent. The fractured surface is glassy and occasionally iridescent.

Other properties.—Very brittle, almost odorless, and the taste is mucilaginous.

Powdered acacia:

Form.—Angular microscopic fragments with but slight traces of starch or vegetable tissues present.

Color.—White.

Solubility.—It is almost completely soluble in twice its weight of water at room temperature, the resulting solution flowing readily and being acid to litmus paper. Acacia is insoluble[2] in alcohol and in organic solvents, and it dissolves in glycerol. Low grades containing cerasin cannot be dissolved by alkalies.

Tests for identity.—Add 0.2 cc. of diluted lead subacetate T.S. to 10 cc. of a 2 per cent cold aqueous solution of acacia; a flocculent, or curdy, whitish precipitate is immediately produced.

[1] "Pharmacopoeia of the United States," 11th decennial revision, p. 9, 1936.
[2] S. B. Trotman, *Chem. Trade J.*, 82, 500-1 (1928).

A 10 per cent aqueous solution of acacia when examined with the polariscope shows but slight laevorotation.

A blue precipitate[3] is obtained when the gum solution is added to sodium hydroxide in the presence of copper sulfate. The supernatant liquid is colorless.

A turbid gray emulsion is produced when a 35 per cent solution of the gum is shaken with cold Nessler solution. At the boiling point a precipitate is produced immediately.

Acacia contains enzymes, and when 1 drop of hydrogen peroxide solution is added to a mixture of equal volume of a cold 30 per cent solution of the gum and a tincture of guaiacum, a blue color is produced.

Tests for purity.—Add 0.1 cc. of ferric chloride to 10 cc. of a 2 per cent aqueous solution of acacia; no blackish coloration nor blackish precipitate is produced (tannin-bearing gums).

Boil a 2 per cent aqueous solution of acacia and cool: it does not give a bluish or reddish color with iodine (starch or dextrin).

Dissolve 5 g. of powdered or finely ground acacia in about 100 cc. of distilled water in a 250-cc. Erlenmeyer flask, add 10 cc. of diluted hydrochloric acid and boil gently for 15 minutes. Filter by suction, while hot, into a Gooch crucible, previously tared, wash thoroughly with hot distilled water, dry at 100°C. and weigh. The weight of the residue thus obtained should not exceed 0.050 g. (water-insoluble residue).

AGAR[4]

Description and physical properties.

Unground agar:

Form.—Usually in bundles from 3 to 6 dm. in length, consisting of thin translucent, membranous agglutinated pieces 4 to 10 mm. in width; or cut, flaked, or granulated.

Color.—Externally is yellowish-white or brownish-white.

Other properties.—It is tough when damp, and brittle when dry. It has a slight odor and a mucilaginous taste.

Structure.—Granular and somewhat filamentous. A few fragments of the spicules of sponges and a few diatoms; in Japanese agar, the frustules of *Arachnoidiscus Ehrenbergii* Baillon, which are disk-shaped and 0.1 to 0.3 mm. in diameter.

Powdered agar:

Form.—In chloral hydrate T.S. the fragments are transparent, more or less granular, striated, angular, and occasionally containing frustules or diatoms.

[3] S. B. Trotman, *Chem. Trade J.*, **82**, 500-1 (1928).
[4] "Pharmacopoeia of the United States," 11th decennial revision, p. 44, 1936.

Color.—Pale buff.

Solubility.—Agar is insoluble in cold water, but slowly soluble in hot water. Boil 1 part of agar for 10 minutes with 100 parts of water and replace the water lost by evaporation: it yields a stiff jelly upon cooling. Agar is insoluble in alcohol, ether, alkali, and dilute acids.[5]

Test for identity.—Iodine colors some of the fragments of agar bluish-black with some areas reddish to violet.

Test for purity.—A solution made by boiling 0.1 g. of agar in 100 cc. of distilled water upon cooling does not produce a blue color upon the addition of iodine T.S. (starch).

Dissolve about 1 g. of agar in 100 cc. of boiling distilled water and allow to cool to about 50°C. To 5 cc. of the solution add 5 cc. of picric acid T.S.: no turbidity appears within 10 minutes (gelatin).

CHONDRUS[6]

Description and physical properties.

Whole chondrus:

Form.—Appears in matted masses; entire plant from 5 to 15 cm. in length, with a slender stalk from which arises a series of dichotomously branching, more or less flattened segments, emarginate or deeply cleft at the tips, and up to 10 mm. in width; translucent, frequently coated with a calcareous deposit which effervesces with hydrochloric acid; sometimes with sporangia embedded near the apex of the segments (in *C. crispus*) or with sporangia borne on short tuberculated projections or stalks, more or less scattered over the upper portion of the segments (in *G. mamillosa*); somewhat cartilaginous.

Color.—Yellowish-white.

Other properties.—Odor slight, seaweed-like; taste, mucilaginous, saline.

Tests for identity and purity.—Boil 1 part of chondrus for about 10 minutes with 30 parts of water, replacing the water lost by evaporation; the strained liquid forms a thick jelly upon cooling.

When softened in cold water, chondrus becomes gelatinous and transparent, the thallus remaining nearly smooth and uniform, and not swollen except slightly at the tips.

Boil 0.3 g. of the drug in 100 cc. of water for a minute; filter the mixture and cool: the filtrate gives no precipitate on the addition of tannic acid T.S. (gelatin), and no blue color on the addition of iodine T.S. (starch).

[5] W. Garner, *Ind. Chemist*, 3, 341-4 (1927).

[6] "The National Formulary," 6th Ed., pp. 80-1, Am. Pharm. Assoc., Washington, D. C., 1935.

Warm 5 g. of chondrus with 30 cc. of water and 5 cc. of phosphoric acid in a suitable flask. No blue color is developed within 15 minutes in potassium-iodate-starch paper suspended in the flask above the fluid (sulfites). A transient blue color usually indicates a higher sulfite content than a permanent blue color.

GELATIN[7]

Description and physical properties.

Form.—In sheets, flakes, shreds, or as a coarse or fine powder.

Color.—Yellowish or colorless.

Other properties.—It has a very slight characteristic odor and taste. When dry is stable in the air, but when moist or in solution it is subject to bacterial decomposition.

Solubility.—Gelatin is insoluble in cold water, but swells and softens when immersed in it, gradually absorbing from 5 to 10 times its own weight of water. It is soluble in hot water, in acetic acid, and in a hot mixture of glycerine and water. It is insoluble in alcohol, in chloroform, in ether, in benzene, in carbon disulfide, and in fixed or volatile oils.

Test for identity.—An aqueous solution of gelatin (1 in 100) yields no precipitate with cupric sulfate T.S. or mercuric chloride T.S., but is precipitated by a solution of chromium trioxide or by trinitrophenol T.S. Even a very dilute solution of gelatin (1 in 5000) is at once rendered turbid by the addition of tannic acid T.S.

Tests for purity.—A hot solution of gelatin in distilled water (1 in 40) is free from a putrid odor, and is not more than slightly acid to litmus paper. Viewed in a layer 2 cm. in thickness, the solution appears only slightly opalescent.

Place 0.1 g. of gelatin, accurately weighed, in a test tube about 150 mm. in length and having an internal diameter of 15 mm., and add enough distilled water to make the mixture measure exactly 10 cc. at 25°C. Place a stirring rod in the tube and allow it to stand, with occasional stirring, for 6 hr. Place the tube in a bath of boiling water and stir until the gelatin is completely dissolved and the solution thoroughly mixed. At once remove the stirring rod, stopper the tube tightly, and allow it to stand in a refrigerator over night. Place the tube in a bath of ice water for 30 minutes, then allow the temperature of the bath to rise slowly. When the temperature of the bath reaches 10°C. the jelly does not flow when the test tube is laid on its side.

Incinerate 0.5 g. of gelatin: it yields not more than 0.01 g. of ash. Dissolve this ash with the aid of heat in a slight excess of hydrochloric acid and a few drops of nitric acid: the resulting solution, diluted with

[7] "Pharmacopoeia of the United States," 11th decennial revision, pp. 176-7, 1936.

distilled water to a volume of 25 cc., meets the requirements of the test for heavy metals of the Pharmacopoeia.

Heat 15 g. of gelatin with 60 cc. of dilute, arsenic-free hydrochloric acid (1 in 4) in a covered flask until all insoluble matter is flocculated and the gelatin dissolved. Add an excess of bromine T.S. (about 15 cc.), neutralize with ammonia T.S., add 1.5 g. of sodium phosphate, and allow to cool. Add a slight excess (about 30 cc.) of magnesia mixture T.S., allow to stand for 1 hr., filter, and wash with five 10-cc. portions of ammonia T.S., diluted with 3 volumes of distilled water. Drain the precipitate well and dissolve it in dilute arsenic-free hydrochloric acid (1 in 4) to a volume of exactly 50 cc. Subject 5 cc. of this solution to the test for arsenic. The stain, if any, is not more intense than that produced in a test made with similar quantities of the same reagents and 1.5 cc. of the standard arsenic test solution.

Dissolve 20 g. of gelatin in 150 cc. of hot distilled water in a flask having a round bottom and a long neck, add 5 cc. of phosphoric acid and 1 g. of sodium bicarbonate, and at once connect the flask with a condenser. Distill 50 cc., receiving the distillate under the surface of 50 cc. of tenth-normal iodine. Acidulate the distillate with a few drops of hydrochloric acid, add 2 cc. of barium chloride T.S., and heat on a water bath until the liquid is nearly colorless. The precipitate of barium sulfate, if any, when filtered, washed and ignited, weighs not more than 0.003 g., corresponding to not more than 0.004 per cent of sulfur dioxide, correction being made for any sulfate which may be present in 50 cc. of the tenth-normal iodine.

Note: Gelatin to be used in the manufacture of capsules in which to dispense medicines may contain not more than 0.15 per cent of sulfur dioxide.

LINSEED—FLAXSEED[8]

Description and physical properties.
Unground linseed:

Form.—Appears as ovate or oblong-lanceolate, flattened, obliquely pointed at one end, from 4 to 6 mm. in length.

Color.—Externally brown, smooth and shiny; raphe a distinct yellow ridge along one edge, the hilum and micropyle in a slight depression just below the pointed end; internally light yellow or brownish.

Other properties.—Oily, odor slight, and taste is mucilaginous and oily.

Structure.—Epidermis with a mucilaginous outer wall covered by a very thin, more or less broken sheath of cutin; two layers of parenchyma

[8] "Pharmacopoeia of the United States," 11th decennial revision, pp. 202-3, 1936.

overlying a continuous layer of stone cells; a pigment layer, with its cells having reddish-brown contents; endosperm of from 6 to 10 rows of cells, surrounding two large, plano-convex cotyledons, cells of cotyledons and endosperm containing a fixed oil and aleurone grains.

Powdered linseed:

Form.—Consists chiefly of large oil globules and irregular fragments of endosperm and seed-coat; seed-coat is characterized by tabular pigment cells filled with reddish-brown amorphous contents and by the somewhat radially elongated stone cells with yellowish, porous walls and rather large lumina; aleurone grains from 0.003 to 0.020 mm. in diameter.

Color.—Yellowish-brown.

Linseed meal:

Form.—The fragments of both seed-coat and kernel, mostly very coarse and with the same cellular tissues as those of the powder.

Color.—Yellow with numerous brown fragments.

Test for purity.—Boil 50 cc. of distilled water with 1 g. of fat-free linseed powder or meal, filter the cooled mixture, and add iodine T.S. to the filtrate: not more than a faint blue color develops in the mixture (starch or starch-bearing seeds).

Assay.—Proceed as directed for the determination of non-volatile, ether-soluble extractive, using 4 g. of ground or powdered linseed, and treat this anhydrous extractive as directed under saponification value.

Volatile ether-soluble extractive.—Extract completely 2 g. of the prepared drug, dried over sulfuric acid for not less than 12 hr., by subjecting it, during 20 hr., to the action of absolute ether in a continuous extraction apparatus. Transfer the ethereal solution to a tared porcelain dish and allow it to evaporate spontaneously. Then dry it over sulfuric acid during 18 hr., and weigh the total ether extract. Now heat the extract gradually up to 110°C. until the weight becomes constant: the loss in weight during the heating represents the volatile portion of the extract.

Non-volatile ether-soluble extractive.—Proceed as directed under Volatile ether-soluble extractive. The weight of the extract after drying in a desiccator and then at 110°C. until of constant weight represents the non-volatile portion of the extract.

Saponification value.—The saponification value is the number of milligrams of potassium hydroxide required to neutralize the free acids and saponify the esters contained in 1 g. of a fat, fatty or volatile oil, wax, resin, balsam or similar substance. It is determined as follows: Place from 1.5 to 2 g. of the sample, accurately weighed, in a flask of from 200- to 250-cc. capacity, and add to it exactly 25 cc. of alcoholic half-normal

potassium hydroxide. Insert into the neck of the flask, by means of a perforated stopper, an air condenser consisting of a glass tube from 70 to 80 cm. in length and from 5 to 8 mm. in diameter, and heat the flask on a water bath for half an hour, frequently rotating the contents. Then add 1 cc. of phenolphthalein T.S. and titrate the excess of potassium hydroxide with half-normal hydrochloric acid. Make a blank test at the same time, using exactly the same amount of alcoholic half-normal potassium hydroxide. The difference in the number of cc. of half-normal hydrochloric acid consumed in the actual test and in the blank test, multiplied by 28.06 and divided by the weight of sample taken, gives the saponification value.

If the oil has been saturated with carbon dioxide for the purpose of preservation, it should be exposed in a shallow dish in a vacuum desiccator for twenty-four hours before the portions are weighed for this determination.

TRAGACANTH[9]

Description and physical properties.

Unground tragacanth:

Form.—Appears in flattened, lamellated, frequently curved fragments or in straight or spirally twisted linear pieces from 0.5 to 2.5 mm. in thickness, and is translucent and horny.

Color.—Whitish or yellowish-white.

Other properties.—Fracture short; rendered more easily pulverizable by heating to 50°C.; inodorous; taste insipid, mucilaginous.

Structure.—A mass showing the distorted and swollen lamellae of mucilaginous walls and a few starch grains.

Powdered tragacanth:

Form.—Angular fragments of mucilage with circular or irregular lamellae; starch grains from 0.003 to 0.025 mm. in diameter, spherical to elliptical, with occasional 2 to 4 compound grains, many of the grains being swollen and more or less altered. The powder shows few or no fragments of lignified vegetable tissue (Indian gum).

Color.—White.

Tests for identity and purity.—Add 1 g. of tragacanth to 50 cc. of distilled water: it swells and forms a smooth, nearly uniform, stiff, opalescent mucilage free from cellular fragments.

Boil 1 g. of tragacanth with 20 cc. of distilled water until a mucilage is formed, then add 5 cc. of hydrochloric acid, and again boil the mixture for 5 minutes; it develops no pink or red color (Indian gum).

[9] "Pharmacopoeia of the United States," 11th decennial revision, pp. 411-12, 1936.

Identification of Gums

Numerous procedures have been written for the separation and identification of the gums by means of group reagents.

Jacobs' and Jaffe's[10] method for identifying the gum consists of noting the behavior of the gums in water, the color reactions, and the types of precipitates produced by the addition of standard reagents, as well as the division of the gums into groups by which ultimate identification is facilitated.

Table 35 shows the behavior of the gums in water.

Table 35. Behavior of Gums in Water

Gum	No. and Form of Samples	Test Solution %	Manner of Solution
Arabic: acacia, arabin	1 Powder 3 Lump	1	Goes readily into clear solution
Tragacanth: bassorin, tragacanthin	2 Powder	1	Swells when placed in water and forms translucent somewhat viscous solution which becomes ropy on standing
Agar	2 Strip form	0.5	Goes into solution on warming, and on cooling forms gel
Karaya: Indian gum	1 Powder	1	Not very soluble in water. Particles swell and form layer at bottom of container
Irish moss: algin	2 Seaweed	0.5 approx.	Translucent, viscous, yellowish solution
Quince seed	2 Seed	1	Opalescent solution and stringy precipitate on standing
Locust kernel: locust bean	5 Powder 1 Extracted from a food	1	Does not form a clear solution. Swells considerably forming opaque colloidal solution from which flocculent precipitate settles on standing

Table 36 gives the results obtained by using standard reagents.

Procedure: Add 2 or 3 drops of the reagent to 5 cc. of the test solution and note the results. Then add an excess of the reagent. When the reagents potassium hydroxide, sulfuric acid, phosphoric acid, hydrochloric acid, Schweitzer's reagent, and neutral ferric chloride are used, a few drops are added to the test solution and the mixture then boiled. An excess of

[10] M. B. Jacobs and L. Jaffe, *Ind. Eng. Chem., Anal. Ed.*, 3, 210-12 (1931).

reagent is then added, and the mixture is re-boiled. When Schiff's reagent is used, the test solution is boiled first, and then the reagent is added. A pink coloration is obtained in each case with Schiff's reagent. This is disregarded, and only a precipitate formation is noticed.

Preparation of Reagents

Borax solution (4 per cent): Dissolve 4 g. of borax in 70 cc. of water and dilute to 100 cc.

Chlorzinciodide: To 100 cc. of solution of zinc chloride (sp. gr. 1.8) add a solution of 10 g. of potassium iodide and 0.15 g. of iodine in 10 cc. of water (keep a few crystals of iodide in the solution).

Ferric chloride (5 per cent): Dissolve 55 g. of ferric chloride in enough of a mixture of 25 cc. of hydrochloric acid and 975 cc. of distilled water to make 1000 cc. of solution.

Iodine solution: Dissolve 2 g. of iodine and 6 g. of potassium iodide in 100 cc. water.

Lead acetate (20 per cent): Dissolve 20 g. of lead acetate in water and make up to 100 cc.

Lead acetate (standard basic solution): Activate litharge by heating it to 650 to 670° for 2.5 to 3 hours in a muffle. (The cooled product should be lemon color.) In a 500-ml. Erlenmeyer flask provided with a return condenser boil 80 g. of normal lead acetate crystals and 40 g. of the freshly activated litharge with 250 g. of water for 45 minutes. Cool, filter off any residue, and dilute with recently boiled water to a density of 1.25 at 20°.

Methylene blue: 0.1 per cent solution in alcohol.

Methylene blue: 0.1 per cent solution in water.

Millon's reagent: Treat 2 ml. of mercury in a 200-ml. Erlenmeyer flask with 20 ml. of nitric acid. Place flask under hood, and after first violent reaction is over shake as much as necessary to effect subdivision of mercury and maintain action. After about 10 minutes, when action has practically ceased even in presence of undissolved mercury, add 35 ml. of water, and if basic salt separates, add sufficient quantity of the dilute nitric acid to dissolve it. Add 10 per cent solution of sodium hydroxide dropwise with thorough mixing until the curdy precipitate that forms after the addition of each drop no longer redissolves but disperses to an evidently permanent turbidity. Add 5 ml. of the dilute nitric acid and mix well. As the solution deteriorates, do not use it after the first day.

Ruthenium red: To a few cc. of 10 per cent solution of lead acetate, add enough ruthenium red to produce a wine-red color.

Schiff's reagent: Dissolve 0.2 g. of Kahlbaum's rosaniline hydrochloric acid in about 120 ml. of hot water. Cool, and add 2 g. of sodium sulfite previously dissolved in 20 ml. of water. Add 2.0 ml. of hydrochloric acid,

Table 36. Results of

Gum	Millon's Reagent	Lead Acetate 20% Soln.	Basic Lead Acetate (A.O.A.C.)	Potassium Hydroxide 10% Soln.	Ferric Chloride 5% Soln.	Alcohol Precipitate
Arabic	White, fine, opaque ppt., sol. in excess of reagent	No ppt.	White, curdy ppt. insol. in excess	Faint yellow tinge	Ppt. sol. in excess	Very fine floc., non-adherent, 40 cc. pt. of definite pptn.
Tragacanth	Voluminous flocculent translucent ppt.	Voluminous flocculent ppt., gels	Voluminous ppt., gels	Bright yellow, stringy ppt.	Gelatinizes	Coag. long and stringy, adherent, 10 cc.
Agar	Gelatinizes	Flocculent ppt. gels	Voluminous ppt.	Clarifies soln.	Gelatinizes, heat + excess → ppt.	Heavy, floc., adherent to beaker, 20 cc.
Karaya[a]	White, curdy ppt. settles rapidly	Neg.	Stringy ppt. settles rapidly	Neg.	Ppt. coag. on heating	Fine filamentous particles, non-adherent, 15-20 cc.
Irish moss	Gelatinizes	Flocculent ppt., gels	Voluminous flocculent ppt., gels	Gels	Vol., stringy ppt., gels.	Coag., translucent, stringy, adherent, 20 cc.
Quince seed	Voluminous flocculent yellowish ppt.	Yellowish flocculent ppt., gels	Yellowish vol., flocculent ppt., gels	Stringy ppt.	Stringy ppt.	Coag., short, stringy, non-adherent, 25 cc.
Locust kernel	Gelatinizes	Voluminous ppt., gels	Gels	Slight floc., ppt.	Stringy ppt.	Stringy, clotty, opaque, non-adherent, start, 2 cc., complete, 15 cc.
Ghatti	Fine ppt.	No ppt.	Translucent, floc. ppt.	Neg.	Neg.	Fine floc. ppt., non-adherent

a = Pink with concentrated phosphoric and hydrochloric acids.

dilute solution to 200 ml., and place in the refrigerator at least 24 hr. before using.

Schweitzer's reagent: Add slowly a solution of copper sulfate to a solution of sodium hydroxide, leaving slight excess of sodium hydroxide; separate by filtration the precipitate of copper hydroxide that forms and wash it thoroughly with water. Dissolve wet precipitate in ammonium hydroxide with aid of heat, cool, and filter. Prepare immediately before use and keep in dark.

Stokes' acid mercuric reagent: Mercury is dissolved in twice its

Tests on Various Gums

Borax 4% Soln.	Schiff's Reagent	Schweitzer's Reagent	Stokes Acid Mercuric Nitrate Reagent	Tannic Acid 10% Soln.	Sulfuric Acid Conc.	A.O.A.C. (1940) Tentative tests (see also Table 37 to 41)	Iodine Soln.
Neg.	Neg.	Neg.	White, fine opaque ppt., sol. in excess reagent	Neg.	Neg.	Group IV.—Greenish-brown with conc. H_2SO_4	Neg.
Neg.	Neg.	Stringy ppt. on heating	Voluminous flocculent translucent ppt.	Neg.	Stringy ppt. on heating	Group I.—Blue with chlorzinciodide, bright-yellow on warming with 10% NaOH	Blue
Neg.	Neg.	Neg.	Gelatinizes	Neg.	Clarifies soln.	Group II.—Opaque blue-black with tincture of iodine, stains with Ruthenium Red	Neg.
Neg.	Neg.	Neg.	White, curdy ppt. settles rapidly	Ppt.	Ppt.	Group III.—Swells considerably and strongly stained pink masses with Ruthenium Red, pink on heating with conc. HCl	Neg.
Neg.	Neg.	Neg.	Gelatinizes	Neg.	Neg.	Group I.—Brown (small blue particles) with chlorzinciodide. Group II.—Brown or lilac with tincture of iodine, characteristic blue stain with alcoholic Methylene Blue	Neg.
Neg.	Stringy ppt.	Stringy ppt. on heating	Voluminous, flocculent, yellowish ppt.	Ppt.	Stringy ppt.	Group I.—Blue with chlorzinciodide, on warming with 10% NaOH gives negative test	Neg.
Gels	Neg.	Neg.	Gelatinizes	Ppt.	Ppt.	Group IV.—Pink or red-brown with conc. H_2SO_4	Neg.
Neg.	—	—	No ppt.	—	—	—	—

weight of nitric acid and diluted to 25 times its volume with water.

Tannic acid (10 per cent): Dissolve 10 g. of tannic acid in 10 cc. of alcohol and dilute to 100 cc.

Dilute acetic acid must be added to the test solution prior to the addition of tannic acid.

Table 37 divides the gums into groups.

Procedure: Add 0.5 cc. of Millon's reagent to 3 cc. of the unknown solution. After a 5 minute period note the results. The gums are now divided into four groups. Assign the gum to the group to which it cor-

responds, and again add the group reagent to 3 cc. of the test solution. This addition identifies the gum, and verification tests on another 3 cc. portion may be made again if necessary.

When tragacanth is boiled with potassium hydroxide solution, a bright yellow solution and a stringy precipitate develop.

Locust bean gives a purplish coloration with iodine solution, while locust kernel does not produce a coloration. Such a test can be used to distinguish between the two.

Potassium hydroxide jellies Irish moss and a seaweed smell is noticeable.

Agar in solution can be clarified by sulfuric acid when boiled.

Schiff's reagent when mixed with quince seed produces a stringy precipitate which rises to the top.

A pink coloration develops if karaya gum is boiled with either phosphoric or hydrochloric acid. If allowed to stand in either solid or solution form, an acetic acid odor develops.

Table 37. Qualitative Groups of the Gums

The unknown may be arabic, tragacanth, agar, karaya, Irish moss, quince seed, or locust kernel.

To 3 cc. of unknown test solution add 0.5 cc. of Millon's reagent:

Group 1	*Group 2*	*Group 3*	*Group 4*
Gelatinizes	Voluminous flocculent ppt., does not settle	Stringy ppt., settles	Powdery or fine curdy ppt.
Irish moss			
Agar	Quince seed	—	Arabic
Locust kernel	Tragacanth	—	Karaya

To 3 cc. of the unknown test solution add group reagent:

Add borax, 4%	Add KOH	Add borax, 4%	Add phosphoric acid
Locust kernel gels	Tragacanth bright yellow	—	Karaya turns pink
Others neg.		—	Arabic dissolves in excess of Millon's reagent
	Quince seed stringy ppt.	—	

To 3 cc. of test solution add KOH:
Irish moss gels
Agar solution clarifies

The procedure developed by the Association of Official Agricultural Chemists[11] consists of:

Preparation of samples.—Controls: Moisten 1 g. of the dry gum with alcohol, add 100 cc. of water with constant stirring and bring to a boil. To 5 or 10 cc. of the resulting liquid or jelly, add 4 volumes of 95 per cent

[11] "Methods of Analysis of the Association of Official Agricultural Chemists," 5th Ed., Washington, D. C., 1940.

alcohol, mix, and centrifuge to bring the precipitate together in a compact mass. (Some gums, notably acacia and agar, may fail to be thrown down by this treatment. The addition of a few drops of a saturated salt solution should cause rapid flocculation and settling.)

Jellies and lotions.—Stir, and add water if necessary to produce a fluid mass. Treat a portion of the sample with 95 per cent alcohol to precipitate the gum as directed under controls. Remove fatty or oily material if present by washing the precipitated gum with ether, then redissolve in water and reprecipitate.

Table 38.[12] Chlorzinciodide

Characteristics of Tests for Gums

Gum	Original Alcohol Ppt.	Group Reaction	Confirmation Test	Remarks
Tragacanth	stringy, bluish ppt.	blue color	warm with 10% NaOH on steam bath, yellow color	certain gums, Irish moss may yield dull yellow color with NaOH; tragacanth a bright yellow
Starch	white compact	bluish-black	iodine, 0.1 N blue color	tragacanth may yield a faint blue
Quince	stringy, translucent	blue color	above test negative	quince is distinguished from starch and tragacanth by negative reaction
Irish moss	stringy	brown (small blue particles)	characteristic molecular structure with group reagent	old preparation of this gum may fail to show characteristic structure

Table 39.[12] Reagent tincture of iodine*

Characteristics of Tests for Gums

Gum	Original Alcohol Ppt.	Group Reaction	Confirmation Test	Remarks
Agar	white, opaque	opaque blue-black	stains with Ruthenium red	does not dissolve or lose shape when covered with water
Irish moss	stringy	brown or lilac	characteristic blue stain with alcohol, methylene blue	these reactions yielded by old as well as fresh preparations

* Allow tincture to dry on mat, flush off with 95% alcohol and irrigate with water.

[12] J. H. Cannon, *J. Assoc. Official Agr. Chem.*, **22**, 726-8 (1939).

The characteristic reactions of the gums to the individual reagents are given in Table 38 for chlorzinciodide, Table 39 for tincture of iodine, Table 40 for ruthenium red and Table 41 for concentrated sulfuric acid.

Table 40.[12] Reagent Ruthenium red (Group III)

Characteristics of Tests for Gums

Gum	Original Alcohol Ppt.	Group Reaction	Confirmation Test	Remarks
Karaya	fine flocculent compact mass on centrifuging	swells considerably, strongly stained pink granular mass	heat with concentrated HCl, pink color	aqueous methylene blue produces a characteristic blue stain

Table 41.[12] Concentrated sulfuric acid (warm cautiously on steam bath). (Group IV)

Characteristics of Tests for Gums

Gum	Original Alcohol Ppt.	Group Reaction	Confirmation Test	Remarks
Acacia	—	greenish-brown	ppt. completely soluble in water	the complete solution of acacia distinguishes it from most other gums

Trotman[13] states that different gums require different quantities of alcohol to effect their precipitation as shown in Table 42.

Table 42. Effect of Alcohol on Precipitation

Gums Precipitated	Concentrated Alcohol (volume)	Nature of Precipitate
Arabic	2.0	White, flocculent, jelly-like
Tragacanth	2.0	White, flocculent, jelly-like
Indian	2.5	Stringy or pasty
Dextrin	3.0	Fine and sticky
Agar	4.0	Fine

Thorium nitrate and neutral lead acetate were used by Bryant[14] to effect the precipitation of the gums. The results are shown in Table 43.

The procedure consists of adding 10 ml. of the aqueous solution of the gum (1 in 100) and adding 1 ml. of a 10 per cent thorium nitrate solution, stirring, and allowing to stand for 2 minutes. If a gel results, the gum is either pectin or quince seed gum. If no gel results it is not pectin. To

[13] S. R. Trotman, *Chem. Trade J.*, 82, 500-1 (1928).
[14] E. F. Bryant, *Ind. Eng. Chem., Anal. Ed.*, 13, 103 (1941).

differentiate between the two gums, to 10 ml. of the sol, add 1 ml. of 5 *N* acetic acid, then 1 ml. of a 10 per cent thorium nitrate solution, stir, and allow to stand for 2 minutes. If no firm gel results the gum is pectin; if a gel forms it is quince seed gum. To check the reaction, a 10 per cent solution of neutral lead acetate is used and the same procedure carried out as for thorium nitrate.

Of the gums listed in the table, only Irish moss, quince seed, and pectin give precipitates with thorium nitrate. The precipitate from Irish moss is stringy and opaque and easily differentiated, but those from quince seed and pectin are alike, being firm, gelatinous in nature. The pectin precipitate is easily dispersed or in some cases actually dissolves on adding an excess of the thorium nitrate solution or dilute acetic acid; the quince seed precipitate with thorium nitrate is unaffected by this treatment.

Table 43. Reactions of Gums and Related Substances with Thorium Nitrate and Neutral Lead Acetate

Material Used	Thorium Nitrate		Neutral Lead Acetate	
	10% Solution	10% Solution and 5 *N* Acetic Acid	10% Solution	10% Solution and 5 *N* Acetic Acid
Gum arabic	a	a	a	a
Locust bean gum	a	a	Slight thickening	a
Gum tragacanth	a	a	a	a
Irish moss	Stringy, white ppt.	White, granular ppt.	Cloudy	Cloudy
Karaya gum	a	a	a	a
Quince seed gum	Firm opaque gel	Firm gel	Fairly firm gel	Very weak gel, a thickening
Pectin	Firm, transparent gel	Very weak gel, a thickening	Firm, transparent gel	Firm, brittle, clear gel
Agar (0.5 instead of 1%)	Slight haze	a	a	a
Methyl cellulose	a	a	a	a
Starch	a	a	a	a

a = No apparent reaction.

A method for identifying several gums by a fluorescence reaction was developed by Radley.[15]

To carry out the test, put 0.1 ml. of test solution in a small test tube, add 1 ml. reagent, mix and heat until the liquid begins to darken. Leave for 2 minutes, cool, examine under ultra-violet lamp, then dilute with 4 ml. of water, cool and re-examine. In the presence of 4 mg. of formalde-

[15] J. A. Radley, *Analyst*, 69, 15-16 (1944).

hyde in 0.1 ml. of test solution, a dull greenish-yellow and a greenish-yellow fluorescence are observed in the concentrated and dilute liquids, respectively. Other aldehydes do not react, nor do the various natural gums, carbohydrates, dextrins, monohydric alcohols or formic, citric or oxalic acid. Tartaric acid, oil, fat, glycerol, and ethylene glycol give a similar reaction when 0.1 ml. of a 0.1 per cent solution is taken for the test, and with these compounds, the examination of the concentration reaction mixture is of some assistance in distinguishing between them as they show yellowish-blue, bright, slightly greenish-yellow, and golden-yellow fluorescence. The fluorescence colors shown on dilution are all similar to that given by formaldehyde. By treating 0.4 ml. of a solution of certain polyhydroxide compounds with a crystal of ammonium persulfate and 2 drops of 1:4 sulfuric acid on a boiling water bath for 5 minutes, then adding 1 ml. of the above reagent boiling 5 seconds, cooling and examining under lamp, results were obtained as given in Table 44.

Table 44. Fluorescence of the Gums

Substance	Concentration Reaction Mixture	Dilute Reaction Mixture
Formaldehyde	Bright greenish-yellow	Strong deep greenish-yellow
Citric acid	Bright strong yellow-green	Bright greenish-yellow
Gum Senegal or arabic	Dull reddish-brown	Strong dull, bluish-green (like lubricating oil)
Tragacanth	Bright greenish-yellow	Weak, greenish-yellow
Ghatti	Strong greenish-brown	Powerful bluish, olive-green
Sodium alginate	Bright yellow	Very faint milky-blue
Carbitol	Powerful yellowish-green	Weak milky-blue

Under these conditions ethylene glycol, glycerol, tartaric acid, glucose, sucrose, starch, dextrin (yellow potato) and oxalic acid give dull shades of greenish-blue in the concentration reaction—in dilute reaction, give only a faint milky-blue fluorescence color.

Solutions of 5 per cent of arabic were identified by Ritsema[16] by the following tests. A brown gel formed upon the addition of ferric chloride, a colorless gel was obtained with borax, a white precipitate with ethyl alcohol, a precipitate with basic lead acetate (sensitive to 1:10,000) and peroxidose test with benzidine and hydrogen.

Rosenthaler[17] precipitated the carbohydrates and glucosides by alkaloidal precipitants. The behavior of starches (0.4 per cent paste), dextrin (10 per cent), glycogen (0.5 per cent), inulin (1, 10 per cent), sugars, arabic (10 per cent), tragacanth (0.5 per cent), agar (0.25 per cent), mucilages of Irish moss, flaxseed, marshmallow, squill, etc., toward

[16] C. Ritsema, *Pharm. Weekblad*, 72, 105-6 (1934).
[17] L. Rosenthaler, *Pharm. Acta Helv.*, 3, 93-6 (1928).

hydrogen bromide-bromine (HBr-Br) (respectively 25 to 10 per cent) (B), tannin (1 per cent) (T), silicotungstic acid (10 per cent) (S) and phosphomolybdic acid (P) is recorded. No precipitates are produced with inulin and sugars. Starches precipitate with B, P and S and become turbid with T; dextrin clouds with T at once, slowly with B, precipitates with S; agar faintly clouds with T, strongly with B and precipitates with P and S; flaxseed is precipitated with T and S, not precipitated with B and P. Glucosides, arbutin, methyl arbutin, salicin, coniferin and esculin, loganin, amygdalin and linamarin gave no precipitates. A 5 per cent aloin solution was precipitated by P and S. The complex glucosides, e.g., convallamarin, digitalin, gitalin, strophanthin (Merck), are precipitated by T, P and S: purest *Gypsophila* saponin is precipitated by P and S, not by T or B. With starches, a chemical explanation of the cause of precipitation is possibly the basic character of the bridging oxygen in their molecule, especially when the relative number of "acid" alcohol groups in the molecule is diminished by polymerization, as in maltose anhydride.

Ewe[18] states that when papain is added to an Irish moss decoction at room temperature, a ropy, gelatinous, insoluble mass separates out; this action is progressively lessened as the papain solution is progressively more highly alkalinized. This action is not prevented by the addition to the papain solution of sodium benzoate, sodium acetate, sodium tetraborate, magnesium sulfate, ammonium sulfate, sodium sulfate, sodium succinate, zinc phenolsulfonate, and Rochelle salt. Sodium thiosulfate, sodium orthophosphate, sodium chloride, potassium chloride, ammonium chloride, sodium glycerophosphate, and especially neutral potassium tartrate reduce the flocculating action of papain. Papain solution also flocculates "solutions" of karaya, quince seed mucilage, sodium alginate, locust bean gum, and agar; it does not produce striking results when added to "solutions" of acacia, tragacanth, gelatin or sassafras pith mucilage. When proteolytic activation of papain is assured by using hydrogen sulfide water for making its solutions, the same results are obtained. The cause of the precipitating action is not established.

Rosenthaler[19] tested samples of tragacanth with guaiac, aloin, pyramidone and benzidine. They gave negative test for oxidases, but strained mucilage (1:100) made from the better grades gave a blue coloration with benzidine and hydrogen peroxide of varying intensity (peroxidase). The presence of protein was detected, especially in the darker sorts, with Millon's reagent, as also with vanillin-hydrochloric acid.

Bruyere's[20] reaction of metaldehyde is applicable to the carbohydrates.

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[18] G. E. Ewe, *J. Am. Pharm. Assoc.*, **30**, 19-20 (1941).
[19] L. Rosenthaler, *Pharm. Zentralhalle*, **65**, 709-10 (1924).
[20] P. Bruyere, *Bull. soc. chim. biol.*, **8**, 462-3 (1926).

He titurated metaldehyde with a drop of concentrated sulfuric acid in the presence of guaiacol. A very sensitive red coloration developed. Sucrose and inulin give almost exactly the same color, grenadine-red. Raffinose and stachyose give a very similar color, whose intensity appears to be due to the presence of fructose radicals. Lactose, maltose and glucose give a fresh rose color. Starch and cellulose gels, lignocellulose, and pecto-cellulose also give the latter tint, provided the tituration be prolonged before the addition of guaiacol. The rose color is also given by the pentosans, gum arabic, and gum tragacanth.

Manseau[21] distinguishes powdered gum tragacanth from powdered acacia by testing with iodine. Tragacanth contains enough starch to give a blue color with iodine solution and acacia contains no starch.

Some reactions for the detection of sizing agents on rayons and staple rayon have been developed by Ohl.[22] Procedure: A sample is extracted with petroleum ether for 3 to 4 hours. The ether is distilled off and the residue treated with alcohol potassium hydroxide. If complete solution occurs with excessive foaming, a saponifiable fat is present. Glycerol may be determined by the formation of acrolein: A large sample (20 g.) is soaked in 500 cc. distilled water at 60° for 4 hr., the solution is poured off and the sample washed with 200 cc. distilled water. The solutions are combined, filtered, and evaporated nearly to dryness. A little potassium acid sulfate ($KHSO_4$) is added and the mixture warmed. In the presence of glycerol the penetrating odor of acrolein may be recognized. Addition of rosaniline sulfate at room temperature gives a blue color. In the hot aqueous extract the following may be determined: Dextrose gives the red copper oxide on warming with Fehling's solution; dextrin gives a wine-red to violet turbidity with I-KI solution which disappears on warming; starch turns dark blue with I-KI which disappears on warming; tragacanth gives a colorless jelly-like precipitate with lead acetate; gelatin and glue give a white precipitate to turbidity with mercuric chloride; protein gives a white precipitate which turns rose-yellow on boiling with Millon's reagent (1 g. of mercury completely dissolved in 9 cc. concentrated nitric acid and 20 cc. of distilled water added); Iceland moss gives a flocculent, jelly-like precipitate with ethanol and British gum a white, jelly-like precipitate with lead acetate.

Methods

There are no convenient methods of determining the various constituents, and the technical evaluation is based upon the viscosity of the solu-

[21] Manseau, *Union pharm.*, **79**, 65 (1928); *Anales. farm. bioquim.* (*Buenos Aires*) *Supl.*, **9**, 10 (1938).
[22] F. Ohl, *Kunstseide u. Zellwolle*, **20**, 230-1 (1938).

tion as compared to that of a standard sample known to be suitable for the purpose. In addition, it is advisable to ascertain the per cent of moisture, acidity, and ash, noting also the color, odor, amount of dirt present, and the keeping qualities of the mucilage.

1. Acid.[23]

Volatile acid is determined by distilling the aqueous solution with phosphoric acid until little is left. It is cooled, and more water is added. It is redistilled, this being repeated until no more acid comes off. The combined distillates are titrated with decinormal sodium hydroxide. The results are expressed in cc. of alkali required by 1 g. of the gum. Examples: arabic < 1 cc.; tragacanth 3 cc.; Indian gum 10 to 20 cc.

2. Acidity.[23]

Titrate 100 cc. of a 5 g. per liter solution with N/2 sodium hydroxide, the acidity being calculated as the milligrams of sodium hydroxide required by 1 g. of the gum.

3. Alginic acid per cent.[23]

The per cent of alginic acid present in a commercial algin sample may be determined by acidifying the neutral or alkaline solution, filtering off, and weighing the precipitate formed.

4. Arabic (gum per cent).[24]

Direct examination of arabic. A solution is made by dissolving 50 g. of copper acetate in water, adding an excess of ammonia and diluting to 1 liter with water and alcohol in such a manner that 50 per cent of the latter is present. For each test 50 cc. of the gum solution (0.25 g. gum) are mixed with 50 cc. of alcohol and 25 cc. of the reagent, mixed and stirred. The precipitate is collected in a Gooch filter, washed successively with ammoniacal 50 per cent, 75 per cent, and 95 per cent alcohol, dried, and weighed. The crucible is ignited and weighed again. The difference between the two weights gives the weight of arabic.

5. Arsenic (in gelatin).[25]

6. Ash.[26]

Method 1: Heat 5 to 10 g. of the sample in 50 to 100 ml. platinum dish at 100° until the water is expelled, add a few drops of pure olive oil, and heat slowly over the flame until swelling ceases. Place dish in a muffle furnace at approximately 525° and leave it until a white ash is obtained. Moisten the ash with water, dry on a steam bath and then on a hot plate, and re-ash at 525° to constant weight.

[23] W. Garner, *Ind. Chemist*, 3, 341-4 (1927).
[24] S. R. Trotman, *Chem. Trade J.*, **82**, 525-7 (1928).
[25] "Methods of Analysis of the Association of Official Agricultural Chemists," 5th Ed., p. 387, Washington, D. C., 1940.
[26] "Methods of Analysis of the Association of Official Agricultural Chemists," 5th Ed., p. 487, Washington, D. C., 1940.

Method 2: Carbonize 5 to 10 g. of the sample in 50 to 100 ml. platinum dish at approximately 525° and treat charred mass with hot water to dissolve the soluble salts. (In case of low-purity products, the addition of a few drops of pure olive oil, as in the previous procedure, may be desirable.) Filter through ashless filter, ignite filter and residue to a white ash, add filtrate of soluble salts, evaporate to dryness, and ignite at about 525° to constant weight.

7. Ash (sulfated).

Weigh 5 g. of a sample into 50 to 100 ml. platinum dish, add 5 ml. of 10 per cent sulfuric acid, ignite until the sample is well carbonized, and then burn in a muffle at about 550°. Cool, add 2 to 3 ml. of 10 per cent sulfuric acid, evaporate on a steam bath, dry on a hot plate, and again ignite at 550° to constant weight. Express result as percentage of sulfated ash.

8. Barium sulfate (in gelatin).[27]

9. Copper (in gelatin).[28]

10. Dextrin (per cent).

Strepkov[29] developed a procedure for the determination of carbohydrates of the second group. The procedure is as follows:

Take 2 cc. of dextrin solution containing not less than 0.1 per cent of dextrin, add 2 cc. of ammonium molybdate reagent and heat for 3 hr. in boiling water bath. Cool quickly and titrate with 0.01 *N* potassium permanganate. The dextrin is calculated as follows: $x = (a + 0.25)/0.75$, where a = cc. of 0.01 *N* potassium permanganate. Determination of gum: Treat an aliquot of a solution containing 0.2 to 3.0 mg. of gum as in the determination of dextrin. The gum is calculated as follows: $x = (a + 0.12)/1.93$, where a = cc. 0.01 *N* potassium permanganate. Determination of dextrin and gum in the same solution: Titrate 1 cc. of the solution with potassium permanganate as in the determination of gum. Then separate the gum from 25 cc. of solution by precipitating with basic lead acetate. Filter off the precipitate and wash with 8 to 10 cc. water. Remove excess lead in the filtrate with sodium sulfate. Filter into a 50-cc. volumetric flask, and wash the lead sulfate precipitate with 8 to 10 cc. of water. Dilute the filtrate to 50 cc. and determine the dextrin in this filtrate. Determine the gum content by difference. The method applied to plant extracts gives values for gum within 2 to 20 per cent of the true values and for dextrins within 0.4 to 1.0 per cent.

11. Metals, heavy (in gelatin).[30]

[27] "Pharmacopoeia of the United States," 11th decennial revision, pp. 176-7, (1936).
[28] J. H. Cannon, *J. Assoc. Official Agr. Chem.*, 22, 726-8 (1939).
[29] S. M. Strepkov, *Botan. Arch.*, 38, 294-302 (1936).
[30] "Pharmacopoeia of the United States," 11th decennial revision, pp. 176-7, 447, 1936.

Incinerate 0.5 g. of gelatin; it yields not more than 0.01 g. of ash. Dissolve this ash with the aid of heat in a slight excess of hydrochloric acid and a few drops of nitric acid: the resulting solution, diluted with distilled water to a volume of 25 cc., meets the requirements of the test for heavy metals. Acidulate 10 cc. of a solution of the substance in distilled water (1 to 50), contained in a test tube of about 25-cc. capacity and about 2 cm. in diameter, with 1 cc. of diluted hydrochloric acid (unless otherwise directed). Warm to about 50°C., add an equal volume of freshly prepared hydrogen sulfide T.S., stopper, and allow the mixture to stand at 35°C. for 10 minutes. At the end of this time the mixture should still possess the odor of hydrogen sulfide; if it does not, thoroughly saturate it with that gas and set the mixture aside again for half an hour. The color produced, if any, is not more intense than that observed in a blank test, made in the same manner, and with the same quantities of the reagents (omitting the solution to be tested), the solutions being viewed crosswise by reflected light while held against a white surface. The test tubes in which the tests are made must be of the same diameter and must match in all other respects, as closely as possible. A slight turbidity owing to separation of sulfur from the hydrogen sulfide may occur. Filter the solution if necessary and render it alkaline by the addition of ammonia T.S.: a greenish color may be produced but no precipitate is formed within one minute. The addition of ammonia T.S. is omitted in testing salts which produce precipitates when ammonia T.S. is added to their solutions.

12. Moisture.[31]

Use a flat-bottomed metal dish about 55 mm. in diameter and provided with tightly fitting slip-in cover. Heat dish and cover to constant weight at 100°, cool, and weigh. Add about 2 g. of prepared sample, cover loosely, and reweigh. Place dish uncovered in water-jacketed oven and dry for 6 hours at temperature of boiling water. Press cover firmly in place, remove dish from oven, cool in vacuum desiccator over sulfuric acid, and weigh. In releasing the vacuum, admit incoming air through the sulfuric acid. Report loss in weight as moisture.

13. Mucilage (per cent in Irish moss).[32]

Analysis of Irish moss: A measured volume of the solution containing approximately 0.2 g. of dry extract, is diluted to 100 cc. acidified with a few drops of 4 *N* hydrochloric acid, and treated with 100 cc. of benzidine chloride containing 4 g. of benzidine and 5 cc. of concentrated hydrochloric acid in 2 liters. After standing 20 minutes, filter the precipitate, wash

[31] "Methods of Analysis of the Association of Official Agricultural Chemists," 5th Ed., p. 386, Washington, D. C., 1940.

[32] S. R. Trotman, *Chem. Trade J.*, **82**, 601-2 (1928).

with a saturated aqueous solution of benzidine sulfate, until free of chlorine. The filter paper plus the precipitate are put into a beaker, 250 cc. of water is added and heated to 80°C. It is titrated with N/10 sodium hydroxide solution using phenolphthalein as an indicator. One cc. N/10 sodium hydroxide = 0.0324 g. of mucilage.

14. Nitrogen (Kjeldahl method).[33]

15. Phosphorus (total).[34]

16. Saponification equivalent.[35]

Saponification equivalent denotes the number of milligrams of sodium hydroxide required to saponify 1 g. of the gum.

A measured volume of the solution is neutralized with decinormal sodium hydroxide using phenolphthalein as an indicator. A measured excess of alkali is added, boiled under a reflux for 1 hour. After cooling, the unused hydroxide is determined by titration.

17. Sugars (in gums).[36]

One g. of the gum is boiled with 200 cc. of dilute sulfuric acid under reflux for several hours. The solution is evaporated to dryness, after neutralization with calcium carbonate and filtered. Add water to the residue, evaporate, and extract with alcohol. Filter the alcoholic solution to remove traces of the gummy matter. Evaporate the alcohol, add 10 cc. of water together with 1 cc. of 10 per cent phenylhydrazine hydrochloride solution in glycerine, and ½ g. of sodium acetate in a test tube. Heat the mixture in water bath for half an hour, filter while hot. Cool, the osazone crystallizes out and may be identified microscopically.

18. Swelling factor (of psyllium seed).

Clevenger[37] has proposed to determine the swelling factor of the seeds as follows: (Method A); introduce 1 g. of seeds in a 10-cc. graduated cylinder (use a 50-cc. cylinder for *Lallemantia royeleana*), fill with water, shake frequently to facilitate the swelling of the mucilage, after 30 minutes allow the seeds to settle and note the total volume occupied by the swollen seeds. Youngken has suggested that the following modification (Method B) permits the formation of more mucilage and therefore serves as a better index of the mucilage-forming capacity: place 1 g. of seeds in a 50-cc. graduated cylinder and add tap water to the 20-cc. mark (to the 50-cc. mark for *Lallemantia royeleana*), shake at intervals during a period of 24 hours, allow to settle and note the total volume occupied by the seeds. Collaborative study indicated that Method B gives considerably higher

[33] "Methods of Analysis of the Association of Official Agricultural Chemists," 5th Ed., pp. 26-27, Washington, D. C., 1940.

[34] "Methods of Analysis of the Association of Official Agricultural Chemists," 5th Ed., p. 387, Washington, D. C., 1940.

[35] S. R. Trotman, *Chem. Trade J.*, **82**, 501-2 (1928).

[36] J. A. Radley, *Analyst*, **69**, 15-16 (1944).

[37] Clevenger, *Drug. Markets*, **29**, 297 (1931).

swelling factors than Method A because of longer period of exposure, and the use of a larger cylinder prevents packing and insures more thorough agitation. Results obtained by both methods showed considerable variation and indicated that temperature plays a part in the determination and that fermentation must be prevented if possible.

19. Viscosity.[38]

Viscosity measurements can be made on numerous instruments. The methods and apparatus listed in the American Society for Testing Materials are utilized in viscosity determinations of asphalts, rosins, varnishes, petroleum products, house paints, etc., and are also applicable to the gums in general.

(a) Falling Ball Method (ASTM D 301-33 T), consists in noting the length of time required for a ball to fall a definite distance through the liquid being tested which is contained in a glass tube of definite uniform diameter. A definite temperature is maintained throughout the test.

(b) Stormer Viscosimeter.—The viscosity is obtained by recording the load and the time in seconds required to make 100 revolutions.

Viscosity centipoises = 0.0313 x load x (sec.—4.5)

The time value is corrected for friction by subtracting the value 4.5 seconds.

(c) MacMichael Torsional Viscosimeter (ASTM D 115-41). The viscosity is measured by noting the angular distance through which a disk is carried by the fluid as the fluid is rotated in the cup.

(d) Kinematic Viscosity (ASTM D 445-42 T) by means of capillary tubes or suspended level viscosimeters.

The apparatus is calibrated with pure distilled water according to American Society for Testing Materials procedures.

$$\text{Viscosity} = Ct - \frac{B}{t}$$

where

V = the kinematic viscosity in centistokes
C = determined calibration constant for the instrument
t = efflux time in seconds
B = experimental constant determined by the design of the viscosimeter

(e) Acacia gum.[39]—The viscosity of pure and impure gum acacia solutions (1 to 6 per cent) at various pH values and with the electrolytes of blood absent or present could be calculated satisfactorily by the formula of Arrhenius, $\log \eta = \theta C$, where η = the viscosity of a water solution,

[38] H. A. Gardner, "Physical and Chemical Examinations of Paints, Varnishes, Lacquers, and Colors," 9th Ed., Sec. Printing, Institute of Paint and Varnish Research, Washington, D. C., 1940.

[39] S. Went, *Am. J. Physiol.*, **85**, 458-67 (1928).

C = concentration of dissolved particles and θ = viscosity constant. The law of Arrhenius could be applied to mixtures of plasma proteins and acacia and to human blood and acacia, but not to mixtures of human erythrocytes and acacia. In the presence of acacia colloids the dispersion of human erythrocytes was changed, but this change was prevented by the presence of human plasma.

(f) Gelatin.[40]—Place 0.1 g. of gelatin, accurately weighed, in a test tube about 150 mm. in length and having an internal diameter of 15 mm., and add enough distilled water to make the mixture measure exactly 10 cc. at 25°C. Place a stirring rod in the tube and allow it to stand, with occasional stirring for 6 hours. Place the tube in a bath containing boiling water and stir until the gelatin is completely dissolved and the solution thoroughly mixed. At once remove the stirring rod, stopper the tube tightly, and allow it to stand in a refrigerator over night. Place the tube in a bath of ice water for 30 minutes, then allow the temperature of the bath to rise slowly. When the temperature of the bath reaches 10°C., the jelly does not flow when the test tube is laid on its side.

(g) Tragacanth.[41]—Four g. of gum tragacanth are weighed, taking as nearly an average sample as possible, added to 50 cc. of water and allowed to steep for 3 days. It is then diluted to 500 cc. with water, and sieved through fine muslin. The sieved mucilage is allowed to stand for an hour or so, since it takes the mucilage some time to become homogeneous after the addition of the water. The viscosity is then taken in the usual manner with any standard viscosimeter. The time is noted for 50 cc. at 15°C., arabic and Senegal require stronger solutions, and it should be noted that with the insoluble gums, unless the sieving is done carefully, false values may be obtained, owing to small portions of swollen jelly clogging the outlet of the viscosimeter.

If the log of the viscosity in seconds be plotted, the curve obtained is much more nearly a straight line, and for the majority of practical purposes using a strength of gum mentioned, the curve may be used safely.

A = standard sample at P shillings or dollars per cwt.
B = outside sample at Q shillings or dollars per cwt.
50 cc. of (a) per cent solution of A takes
x seconds
50 cc. of (b) per cent solution of B takes
y seconds

100 parts by weight of A gives the same viscosity as

$$\frac{100\ b \cdot \log x}{a \cdot \log x}$$

[40] "Pharmacopoeia of the United States," 11th decennial revision, pp. 176-7, 1936.
[41] W. Garner, *Ind. Chemist*, 3, 341-4 (1927).

parts by weight of B and the equivalent weight of B to give the same viscosity at 100 parts of A will cost

$$\frac{Qb \cdot \log x}{a \cdot \log y} \text{ shillings or dollars}$$

Trotman[42] stated that the viscosity of tragacanth can be determined when 1 g. of the gum is agitated with 2 cc. of alcohol in a 100-cc. flask. It is made up to the mark with water and allowed to stand for 24 hours with frequent shakings. The viscosity is measured. In a good sample, the number of drops formed in 2 minutes should not be more than 30.

Haddock[43] suggested that the comparison between samples of tragacanth be made by comparison of the viscosities of 0.4 per cent aqueous mucilages in poises at 20°. If a gum gives a mucilage with a viscosity above 1.3 poises, it may be regarded as of good quality.

20. Water-insoluble residue (arabic).[44]

Dissolve 5 g. of powdered or finely ground arabic in about 100 cc. of distilled water in a 250-cc. Erlenmeyer flask, add 10 cc. of diluted hydrochloric acid, and boil gently for 15 minutes. Filter with suction, while hot, into a Gooch crucible, previously tared, wash thoroughly with hot distilled water, dry at 100° C., and weigh. The weight of the residue thus obtained should not exceed 0.050 g.

21. Zinc (in gelatin).[45]

Gums which appear on the market are sometimes adulterated with other gums. Various procedures have been determined for detecting their presence.

Trotman[46] states that gums which are rich in arabin dissolve in chloral, those containing cerasin and arabic give a clear solution in 4 to 5 days, and a mucilage or jelly formed by the swollen cerasin. When much bassorin is present only a swollen, cloudy mucilage is produced.

22. Agar (in the presence of gelatin).[47]

The presence of gelatin masks the reaction between agar and iodine. To remove the gelatin freeze the solution and then melt it in a water bath held at 60° C. When melted, centrifuge and pour off the supernatant liquid, wash the residue in water at 60° C., recentrifuge, and place the residue in a small volume of water (10 to 25 cc.) depending on the size of the sample. Bring to a boil and refilter. The filtrate should now contain all the agar. If a yellow color is still given with the iodine solution, all

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[42] S. R. Trotman, *Chem. Trade J.*, **82**, 525-7 (1928).
[43] L. A. Haddock, *Quart. J. Pharm. Pharmacol.*, **7**, 505-8 (1934).
[44] "Pharmacopoeia of the United States," 11th decennial revision, p. 9, 1936.
[45] J. H. Cannon, *J. Assoc. Official Agr. Chem.*, **22**, 726-8 (1939).
[46] S. R. Trotman, *Chem. Trade J.*, **82**, 525-7 (1928).
[47] J. H. Cannon, *J. Assoc. Official Agr. Chem.*, **18**, 552-4 (1935).

the gelatin has not been removed and the procedure should be repeated. By this means agar to the amount of 0.1 per cent has been detected when mixed with 5 per cent of gelatin solution.

23. Cerasin and bassorin (in gums).[48]

Detection of cerasin and bassorin was determined when 40 g. of the sample were soaked in 500 cc. of water at 20 to 22° C. for 24 hours, diluted with 500 cc. of water, mixed and allowed to stand. The clear solution is decanted, the insoluble matter filtered, and boiled with 10 per cent solution of sodium carbonate to dissolve the cerasin. The solution is filtered, acidified slightly with phosphoric acid, and an equal volume of 98 per cent alcohol is added. In the presence of cerasin a white precipitate is produced which may be filtered and weighed. The residue after the treatment with sodium carbonate may contain any bassorin which may be present.

24. Dextrin (in glue).

Alexander[49] states that any dextrin (in glue) may be detected by hydrolyzing the mixed glue with dilute hydrochloric acid and then testing the liquid for dextrose with Fehling's or Benedict's qualitative solution. The protective colloid action of the protein and its hydrolysis tends to make the copper oxide precipitate so fine that it appears yellow, and if all the copper is not reduced the solution may appear green.

25. Indian gum in Smyrna tragacanth procedure.[50]

One g. of gum is soaked in 50 cc. of water. It should give a firm, opalescent homogeneous mucilage free from cell debris. Indian gum produces a mucilage containing reddish particles in suspension.

When 1 g. of the gum is ground with 1 cc. of glycerol, 48 cc. of water added, and the whole mixed, a consistent jelly should be produced which is capable of forming drops requiring at least 10 seconds to fall from the glass rod.

One g. of the gum is macerated for 24 hours with 100 cc. of water. An opaque liquid mucilage should be formed containing fragments of swollen gum. This is filtered through paper. The insoluble residue should give a blue color with iodine, but no starch is present in the filtrate.

Gums in Drugs

Gums are also utilized in the manufacture of pharmaceuticals and cosmetic preparations. Here again the varying nature and the complexity of the preparations make it impossible to devise a method which embraces all of the gums.

26. Acacia (in blood).

[48] S. R. Trotman, *Chem. Trade J.*, 82, 525-7 (1928).
[49] J. Alexander, *Ind. Eng. Chem., Anal. Ed.*, 5, 200, (1933).
[50] S. R. Trotman, *Chem. Trade J.*, 82, 601-2 (1928).

The procedure developed by Peoples and Phatak[51] consists of a spectroscopic determination of gum acacia in blood by precipitating 0.5 to 1.0 cc. of blood according to the Folin-Wu technique. Pipet 0.5 to 2 cc. of the filtrate, sufficient to contain 0.5 to 1.0 mg. of acacia, into a 10-cc. volumetric flask and add distilled water to give a total volume of 2 cc.; add 2 cc. of 80 per cent sulfuric acid; mix and heat in a 100° water bath for exactly 30 minutes and promptly cool to room temperature; add 5 cc. of 80 per cent sulfuric acid and 1 cc. of 1 per cent bile salts in 70 per cent ethyl alcohol; mix and place in a 57° water bath for 20 minutes; cool immediately to room temperature and after at least 10 minutes, and not over 40 minutes, read in a spectrometer. The characteristic absorption band lies between *E* and *b*. A standard, consisting of diluted acacia solution, is treated exactly as the Folin-Wu filtrate; 0.5- and 1.5-mg. standards usually are sufficient. The absorption band and the color tint are always the same regardless of the concentration of acacia; the intensity of the color is accurately proportional to the amount of acacia in the sample. The method is accurate within 5 per cent for 1 to 25 mg. but will detect 0.05 mg. In 5 normal dogs, purified acacia in 20 per cent solution was slowly injected intravenously in doses of 0.5 to 1.5 mg. per kg. of bodyweight; the blood volume was markedly increased and several days were required for the complete elimination of the acacia.

27. Acacia and tragacanth (in drug emulsions).[52]

The analysis of pharmaceutical emulsions covers the determination of oil, gum, protein, soap, etc. Mixtures of gum acacia and tragacanth were determined by Smith and Grinling. The procedure consists of dissolving the precipitated gum mixture in a little water and determining the viscosity. Comparison is then made with viscosities of solutions of the mixtures of the two gums in varying proportions but of equal concentrations.

28. Agar, acacia, Irish moss, quince, and tragacanth in drugs.[53]

When separated from drug mixtures certain gums fail to yield the reactions observed in pure gum suspensions in water. Microscopical examination of the gum after precipitation with alcohol gave promising results. The special microscope accessories found most useful were the polarizer and the dark field illuminator. The reagents used were limited to 95 per cent alcohol saturated with sodium chloride, tincture of iodine, and zinc-chloro-iodide solution (10 g. of potassium iodide and 0.1 g. of iodine dissolved in 100 cc. of 60 per cent zinc chloride solution). Direct examination with dark field illumination shows two general types of

[51] S. A. Peoples and N. M. Phatak, *Proc. Soc. Exptl. Biol. Med.*, **32**, 635-7 (1935).
[52] E. L. Smith and G. N. Grinling, *Pharm. J.*, **125**, 91-2 (1930); *Chemist and Druggist*, 113, 118-9 (1930).
[53] J. H. Cannon, *J. Assoc. Official Agr. Chem.*, **20**, 588-9 (1937).

precipitates: (1) definite stringy structure and (2) tiny noncrystalline particles of uniform size and consistency. Of the gums studied, only agar and acacia fall in (2). Tragacanth, quince seed, and Irish moss appear stringy. Examination in polarized light before and after treatment with zinc-chloro-iodide reveals structural differences between tragacanth, Irish moss and quince seed which apparently can be made the basis of positive identification of these gums.

Procedure.—To a concentrated aqueous solution of the gum suspension add 4 volumes of the salt saturated alcohol solution, mix, and centrifuge. Decant the alcohol from the compacted gum precipitate and cover it with 95 per cent alcohol. Let it stand for an hour to further harden and dehydrate the precipitate. Remove a particle of the solid material to a clean slide and press flat and then place as soon as possible beneath a coverglass. (Examination at this stage with the lower power and with dark illuminator will give considerable information as to the type of gum dealt with.) Carefully remove the glass-cover so as to leave the thin mat of precipitate attached to the slide. Cover the gum with a drop of tincture of iodine, allow the alcohol to evaporate, and cover with a drop of zinc-chloro-iodide. Examine in polarized light from time to time during several minutes.

29. Agar, arabic, and tragacanth (in drugs).[54]

Drop tests were utilized in the examination of pharmaceuticals and were developed by Frehden and Goldschmidt.

Procedure.—Place in a small, high-walled crucible a little of the substance and mix it with about 8 mg. of oxalic acid and a few drops of dilute sulfuric acid. Heat carefully until the reaction starts. As soon as the contents of the microcrucible begin to turn brown, cover the crucible with a small watch glass upon the under side of which is stuck a piece of filter paper that has been impregnated with o-dianisidine in glacial acetic acid. If sugar is present the paper soon assumes a violet tint. Furfurole derivatives are formed as a result of the prolonged heating and these condense with o-dianisidine to form Schiff bases. By this test it was possible to detect 0.05 mg. of *d*-glucose or levulose, 0.1 mg. of sucrose or lactose, 0.01 mg. of amylum sago (sago starch), amylum maranthae, amylum solani or amylum maidis, 0.05 mg. of agar, 0.01 mg. of tragacanth, 0.005 mg. of gum arabic, and 0.01 to 0.02 mg. of cellulose.

30. Agar, Irish moss, karaya, quince, and tragacanth (in drugs).[55]

A collaborative study by Cannon was made on the identification of Irish moss, tragacanth, agar, quince, karaya, by means of zinc-chloro-iodide. (See Identification of Gums.)

[54] O. Frehden and L. Goldschmidt, *Mikrochim. Acta.*, **2**, 184-7 (1937).
[55] J. H. Cannon, *J. Assoc. Official Agr. Chem.*, **18**, 552-4 (1935).

31. Agar and Irish moss (in emulsions and tonic mixtures).[56]

The tonic contained 0.2 per cent Irish moss, 22 per cent alcohol, 8 per cent plant extractive material, water and small amounts of iron, quinine, and glycerine.

The agar emulsion contained 1 per cent agar, water, oleic acid, and liquid petrolatum. The tonic and the agar emulsions served as known materials to check the accuracy of the procedure.

The procedure devised by Cannon consists of: Transfer about 20 cc. of sample to a 400-cc. beaker and add 20 cc. of water. Bring to a boil, add 2 cc. of 10 per cent acetic acid and 3 teaspoonfuls of kieselguhr, and continue boiling for about 2 minutes. Filter while hot through folded filter and discard precipitate to filtrate, add 4 volumes of 95 per cent alcohol, centrifuge until gum has settled, and decant supernatant liquid. Add approximately 30 cc. of 80 per cent alcohol, shake thoroughly, and again centrifuge. Decant alcohol and transfer the gum to a tared beaker with the aid of water. Evaporate to dryness on steam bath, weigh residue and make a 0.2 per cent solution. Test this solution for identity according to the following tests.

For a preparation containing fatty or oily material make an ether extraction using about 50 cc. ether, after the addition of the 20 cc. water and before bringing to a boil. Outline of tests.—To 5 cc. of a 0.2 per cent solution of the gum in a medium sized tube, add reagents in the order named:

Gum	*Reagent*	*Test*
Quince seed	Ammonium molybdate	Opaque, gelatinous ppt. on heating after addition of reagent (other gums negative).
Karaya	Millon's reagent	White ppt. settles on standing 4 to 5 minutes, after addition of 1 drop of reagent (other ppts. do not settle rapidly).
Tragacanth	10% potassium hydroxide	Deep yellow color on boiling after addition of 4 drops of reagent (acacia faint yellow tinge, others negative).
Irish moss	10% ferric chloride	Light colored opaque ppt. forms immediately on addition of 0.5 cc. of reagent (quince yields flocculent ppt.).

[56] J. H. Cannon, *J. Assoc. Official Agr. Chem.*, **18**, 552-4 (1935).

Gum	*Reagent*	*Test*
Agar	10% ferric chloride	Brown flocculent ppt. on heating after addition of 0.5 cc. of reagent (karaya yields similar ppt.).
Acacia	10% ferric chloride	Fine white ppt. forms slowly on addition of 1 drop of reagent (no ppt. formed where an excess is added immediately as in test for Irish moss).

Gums in Foods

Edible gums are being increasingly used in the manufacture of prepared food. In some cases they have a legitimate use, and in many cases they serve to mask adulteration.

Due to the complexity of many prepared foods, and the varying nature of the gums themselves, it is impossible to devise one method for all products and conditions.

Gums may be encountered in a variety of prepared foods. Among them are mayonnaise, French dressing, fruit spreads, and jellies, sirups, dairy drinks, soft cheeses, ice cream, flavor emulsions, and confectionery.

Haas and Russell-Wells[57] state that the method of determining the mucilage in Irish moss can be used in the presence of other mucilaginous substances and should be capable of determining carrageen in jams and jellies. (*See method No. 13*).

32. Agar.

(a) Canned chicken.[58]

The gel separated from the meat is dissolved in water and digested for 1 hour at 38° and pH 2 to 2.5 with 0.1 g. pepsin. Sufficient trichloroacetic acid to make 10 per cent solution is added, and the solution is heated on the water bath until any precipitate which forms is coagulated; 2 volumes of acetone is added to the filtrate, and the precipitate is treated like the like precipitate in the detection of agar in mayonnaise.

(b) Preserves.[59]

By precipitation. Cover 30 g. of jam or jelly with 270 cc. of hot water, stir until thoroughly disintegrated and boil for 3 minutes. Filter immediately, while still boiling hot, through a rapid filter paper. In the presence of agar a precipitate will form upon standing not longer than 24

[57] P. Haas and B. Russell-Wells, *Analyst*, 52, 265-9 (1927).
[58] F. L. Hart, *J. Assoc. Official Agr. Chem.*, 20, 527-34 (1937).
[59] "Technical Methods of Analysis," 2nd Ed., p. 588, McGraw-Hill Book Company, Inc., New York, 1927.

hours. Filter, wash with cold water. Upon chilling this hot water solution a firm jelly will be formed that can be examined by touch. This method will detect 0.2 per cent of agar with certainty if the proportions of jam or jelly and water are strictly observed.

The procedure by King[60] consists of removing the sugar and alcohol-soluble portions of the preserve by treatment with 95 per cent alcohol. Add the alcohol in small portions and with constant stirring until the volume is 300 cc. After heating 1½ to 2 hours, filter, with gentle suction at the last. After washing with alcohol, transfer the residue back to the beaker and again treat with 300 cc. of alcohol as before. Boil the residue a few minutes with 200 cc. of water, filter, wash and repeat the treatment, keeping the liquid above 80°. Concentrate to 300 cc. In 100 cc. determine the free sulfate in the usual way, taking care not to add acid until the last. Call this weight of barium sulfate (a). To the remaining 200 cc., add 100 cc. of concentrated hydrochloric acid and boil for 6 hours, replacing acid as necessary. This hydrolyzes the agar and the two SO_3^{--} groups are converted to SO_4^{--}. Finally concentrate to 25 cc., dilute to 350 cc. and filter. Add barium chloride, allow to stand overnight, filter and weigh. Call this weight (b). Then the per cent agar is $15(1.5(a-2b))$. With this empirical factor, good results were obtained in samples to which agar was added.

(c) Detection of agar.[61]

The color reactions of agar and iodine as given in the Pharmacopoeia of the United States for the detection of agar can be used to distinguish it from the gums usually used in foods. The red coloration given by agar is not given by the common gums such as quince, tragacanth, karaya, Irish moss, and acacia. Use is also made of the solubility of agar in boiling water and its ability to form a gel in the cold when present to the extent of 0.5 to 1.5 per cent.

33. The determination of dextrin in fruits and fruit products, spices, sugar and sugar products, is given in detailed form in the Official Methods of the Agricultural Chemists.[62]

34. The detailed methods for the analysis of gelatin in cheeses such as those of the cottage variety,[62] in coatings on coffee,[63] in ice cream,[64] in jams and jellies,[64] and related materials, as well as the determination of the presence of proteoses and gelatin in meats,[62] are given in the standard

[60] J. King, *Analyst*, **50**, 371-83 (1925).
[61] J. D. Wildman, *J. Assoc. Official Agr. Chem.*, **18**, 637 (1935).
[62] "Methods of Analysis of the Association of Official Agricultural Chemists." 5th Ed., Washington, D. C., 1940.
[63] *J. Assoc. Official Agr. Chem.*, **28**, 97-105 (1945).
[64] R. C. Griffin, "Technical Methods of Analysis," 2nd Ed., p. 587, McGraw-Hill Book Company, Inc., New York, 1927.

text books. Elsewhere in the volume are given the methods of determination of gums in cheese such as those of the soft curd variety, as well as gums in mayonnaise and French dressings. Gums are sometimes found in wines and these are the subjects of detailed procedures.[62]

(a) Foods. The extraction of gums from foods, drugs, and like substances can be done by either the Patrick[65] or Cook and Woodman[66] methods.

To the sample containing the gum, add half the volume of water and boil for a few minutes. Then add 2 cc. of 10 per cent acetic acid for every 50 cc. of sample, heat to boiling, and add 3 teaspoonfuls of kieselguhr for every 50 cc. of the sample. Filter on a plaited filter and discard the precipitate. Precipitate the gum from the filtrate by the addition of 10 cc. of 95 per cent alcohol for every 3 cc. of the filtrate. Add 3 cc. of a mixture of 95 cc. of the 95 per cent alcohol and 5 cc. of concentrated hydrochloric acid. The acidified alcohol completely dissolves the milk proteins. At this point Morris B. Jacobs and Leon Jaffee centrifuged and filtered the alcohol solution containing the precipitated gum, washed the gum with 95 per cent alcohol to free it from the acid, and then allowed the gum to dry spontaneously before applying qualitative tests for its identification.

Dilute the sample to a suitable concentration with water. Add 5 cc. of dilute acetic acid and 25 cc. of 10 per cent tannin solution, heat the mixture for 20 to 30 minutes, centrifuge, filter, and discard the precipitate. Add 40 to 50 cc. more of tannin solution, heat for a short time, centrifuge and filter. Again discard the precipitate. Treat the filtrate with twice its volume of acetone, centrifuge and filter, and discard the filtrate. Dissolve the precipitate in 50 cc. of warm water slightly acidified with acetic acid, and then add 10 cc. of ammonia (sp. gr. 0.90), centrifuge, and filter. Add acetic acid to the filtrate until slightly acid and precipitate the gum with 95 per cent alcohol. At this point Jacobs and Jaffee centrifuged, filtered, and washed the precipitate with 95 per cent alcohol, and then allowed the gum to dry spontaneously before making qualitative tests.

In products which contain no alcohol-insoluble substances, such as proteins, dextrins, etc., other than gums, it is best to precipitate the gums directly. If the sample is liquid, merely add the requisite amount of 95 per cent alcohol. If it be solid, add a suitable amount of water, make slightly acid with acetic acid, boil, and filter. Precipitate the gums from the filtrate with 95 per cent alcohol.

(b) Ice cream. The methods for gums in cheese are applicable to vanilla ice cream. The pectin sometimes present in fruit ice cream may

[65] U. S. Dept. Agr. Bur. Chem. Bull. 116, 26 (1914).
[66] *Ibid,* 10, 520 (1918).

interfere. Positive tests were obtained with as little as 0.2 per cent carob bean or tragacanth.[67]

(c) Mayonnaise and French dressings.[68]

(d) Sirups. (Determination of gums in sirups.)[69]

To 50 cc. of the sirup add 5 cc. of hydrochloric acid and 85 cc. of absolute alcohol, the acid and alcohol being added drop by drop with constant stirring. The precipitate is filtered, washed with alcohol containing 10 per cent hydrochloric acid, and then with absolute alcohol. It is then dried and weighed. The per cent gum is found by adding 16.1 per cent of the weight of the precipitate, this representing the average per cent of water plus ash in the original gum.

(e) Tomato products.[66] Soluble gums in tomato products (catsup, puree, consomme).

35. Karaya and tragacanth (in catsup), determination of:[70]

One drop of catsup is mixed on a microscope slide with one or two drops of water, depending on the consistency of the product. From this diluted material, a small mount is made and examined with a magnification of approximately 100 diameters. Under these conditions the insoluble portions of the gum appear as billowy masses of various shapes and sizes. The gum in water appears almost colorless, but in catsup the protoplasmic particles adhere to the surface of the masses, thus facilitating their identification. When pressure is applied to the cover slip, the specimens show resiliency. When the cover slip is moved along the slide the masses roll over and over. A supplementary test consists of treating one drop of the product with one or two drops of zinc-chloro-iodide reagent. The cellulose of the cell is thereby stained blue, while the gum masses stain somewhat greenish.

Tragacanth. This gum resembles karaya in all of the above points except that the masses tend to be more uniform in shape and size. In addition a small per cent of the masses shows the striation characteristic of tragacanth. Search for these is often tedious, but it is essential to the identification of the gum.

[67] F. L. Hart, *J. Assoc. Official Agr. Chem.*, **20**, 527-34 (1937).

[68] "Methods of Analysis of the Association of Official Agricultural Chemists," 5th Ed., p. 477, Washington, D. C., 1940.

[69] S. R. Trotman, *Chem. Trade J.*, **82**, 525-7 (1928).

[70] J. D. Wildman, *J. Assoc. Official Agr. Chem.*, **18**, 637 (1935).

Chapter 16

Native Designations of the Gums

In view of the many names under which the gums are known in different parts of the world and the confusion caused by many names for the same article, these designations are tabulated. The local name or trade variant is in the first column of Table 45, the geographical place of origin is given in the second column, the botanical source is in the third column, and the present day classification as used in this book is given in the last column. It is hoped that this classification will aid in simplification and standardization of gum designations.

Table 45. Native Designations of the Gums

Name	Place of Origin	Type	Present Day Classification
A			
Abyssinia	Abyssinia	Acacia	Arabic
Acacia	Africa, Near East	Acacia	Arabic
Aden	Africa	Acacia	Arabic
Agar	Continental Sea Coasts and Japan	Seaweed	Agar
Aleppo	Near East	Astragalus	Tragacanth.
Algin	British Isles, Europe, United States, Nova Scotia	Seaweed	Alginate
Angelique	South America	Dicorynia	Karaya substitute
Angico	South America	Piptadenia	Arabic substitute
Anogeissus	India	Anogeissus	Ghatti
Arabic	Africa, Near East	Acacia	Arabic
Arrehbor	Iran (Persia)	Astragalus	Tragacanth
Astragalus	Iran, Asia Minor, Armenia, Kurdistan, Palestine, Irak, British India, Russia, Turkey	Astragalus	Tragacanth
Australian black wattle gum	Australia	Acacia	Arabic
B			
Babool	India	Acacia	Arabic
Balsam	Canada, United States	Resin	Canadian balsam
Barbary, brown	Sudan, Africa	Acacia	Arabic
Bar Kanten	Japan	Seaweed	Agar
Basra	Iran (Persia), Near East	Astragalus	Tragacanth
Bassora	Iran (Persia)	Sterculia	Karaya
Beira	Argentina	Caesalpinia	Karaya substitute
Berbera	Senegal, Africa	Acacia	Arabic
Blanche gomme	Sudan, Africa	Acacia	Arabic
Blonde gomme	Sudan, Africa	Acacia	Arabic
Blonde psyllium seeds	Mediterranean area	Plantago	Psyllium
Brea	Argentina	Caesalpinia	Karaya substitute
Broadleaf kelp	Europe, United States	Seaweed	Alginate
Bushire	Iran (Persia)	Astragalus	Tragacanth
C			
Cactus	United States, Mexico, Central and South America	Cactus	Tragacanth substitute

Table 45—*Continued*

Name	Place of Origin	Type	Present Day Classification
Canada balsam	Canada, United States	Resin	Canadian balsam
Cape	Union of South Africa	Acacia	Arabic
Carmania	Syria	Prunus	Ghatti substitute
Carob	South Europe, North Africa, Mediterranean area	Ceratonea	Locust bean
Carob seed	South Europe, North Africa, Mediterranean area	Ceratonea	Locust bean
Carrageen	British Isles, New England, Europe, Nova Scotia	Seaweed	Irish moss
Carragheen	British Isles, New England, Europe, Nova Scotia	Seaweed	Irish moss
Carrageenin	British Isles, New England, Europe, Nova Scotia	Seaweed	Irish moss
Cashew	India	Anacardiaceae	Arabic substitute
Catechu	India	Acacia	Arabic
Cedar	Central America, West Indies	Cedrela	Cedar
Cedro	Central America, West Indies	Cedrela	Cedar
Cherry	Europe, United States	Prunus	Cherry
Chinese isinglass	Japan, China	Seaweed	Agar
Chironji	India	Buchanania	Karaya
Chitira	Iran (Persia)	Astragalus	Tragacanth
Chittagong	India	Indefinite	Indian
Chondrus	British Isles, North Europe, New England, Nova Scotia	Seaweed	Irish moss
Cutch gum	India	Acacia	Arabic
Cydonium	Near East, Asia, Europe, South Africa, United States	Cydonium	Quince seed
D			
Date gum	Africa	Palm	Date
Dhak	India	Indefinite	Indian
E			
East India gum	India, East Indies	Acacia	Arabic
East Indian gum	Iran (Persia)	Acacia	Arabic
Elephant	India	Indefinite	Indian
F			
Flea seed	Mediterranean area	Plantago	Psyllium
Fleawort	Mediterranean area	Plantago	Psyllium

Table 45—*Continued*

Name	Place of Origin	Type	Present Day Classification
G			
Gatto	South Europe, Africa, Mediterranean area	Ceratonea	Locust bean
Gavan	Iran (Persia)	Astragalus	Tragacanth
Gedda	Africa	Acacia	Arabic
Geddaref	Egypt	Acacia	Arabic
Gehzirah	Africa	Acacia	Arabic
Ghati	India, Ceylon	Anogeissus	Ghatti
Ghatti	India, Ceylon	Anogeissus	Ghatti
Goma de Cedro	Central America, West Indies	Cedrelo	Cedar gum
Goma de Guanacaste	Central America, West Indies	Enterolobium	Arabic substitute
Gomme blanche	Sudan, Africa	Acacia	Arabic
Gomme blonde	Sudan, Africa	Acacia	Arabic
Gomme de Galam	Senegal, Africa	Acacia	Arabic
Gomme de Podor	Senegal, Africa	Acacia	Arabic
Gomme de Tombouctou	Senegal, Africa	Acacia	Arabic
Gomme du bas du fleuve	Senegal, Africa	Acacia	Arabic
Gomme du haut de fleuve	Senegal, Africa	Acacia	Arabic
Gomme fabrique	Senegal, Africa	Acacia	Arabic
Gomme friable	Senegal, Africa	Acacia	Arabic
Guamacho	South America	Cactus	Tragacanth substitute
Guar	India, United States	Legume	Guar
H			
Halusia	Iran (Persia)	Astragalus	Tragacanth
Hashab geneina	Egypt	Acacia	Arabic
Hashab wady	Africa	Acacia	Arabic
Hevo	South Europe, Africa, Mediterranean area	Ceratonea	Locust bean
Hindu tragacanth	India	Sterculia	Karaya
Horsetail kelp	Europe, United States	Seaweed	Alginate
I			
Iceland moss	Iceland, Sweden, Norway	Lichen	Iceland moss
India gum	India	Sterculia	Karaya
Indian gum	India, Ceylon	Anogeissus	Ghatti

Table 45—*Continued*

Name	Place of Origin	Type	Present Day Classification
Indian tragacanth	India	Sterculia	Karaya
Irish moss	British Isles, Europe, United States, Nova Scotia	Seaweed	Irish moss
Isabghol	Mediterranean area	Plantago	Psyllium
Isinglass	Continental Sea Coasts	Seaweed	Agar
J			
Jandagum	South Europe, Africa, Mediterranean area	Ceratonea	Locust bean
Japanese gelatin	Japan	Seaweed	Agar
Japanese isinglass	Japan	Seaweed	Agar
Jeddah	Morocco	Acacia	Arabic
K			
Kadaya	India	Sterculia	Karaya
Kanten	Continental Sea Coasts	Seaweed	Agar
Karai	Iran (Persia)	Astragalus	Tragacanth
Karaya	India	Sterculia	Karaya
Katad	Iran (Persia)	Astragalus	Tragacanth
Kathira	Iran (Persia)	Astragalus	Tragacanth
Katilo	India	Sterculia	Karaya
Katira	Iran (Persia)	Astragalus	Tragacanth
Katira-i-hindi	Iran (Persia)	Sterculia	Karaya
Katya	Iran (Persia)	Astragalus	Tragacanth
Katyra	Iran (Persia)	Astragalus	Tragacanth
Keltex	United States	Seaweed	Alginate
Kettira	Iran (Persia)	Astragalus	Tragacanth
Khartoum	Africa	Acacia	Arabic
Killeen	British Isles, Europe, United States, Nova Scotia	Seaweed	Irish moss
Kino	India	Pterocarpus	Indian gum
Kobe	Japan	Seaweed	Agar
Kordofan	Sudan, Africa	Acacia	Arabic
Kullo	India	Sterculia	Karaya
Kuteera	Asia, Iran (Persia), India	Sterculia	Karaya
Kutera	Iran (Persia)	Astragalus	Tragacanth

Table 45—*Continued*

Name	Place of Origin	Type	Present Day Classification
L			
Lakoe	Africa, South Europe, Mediterranean area	Ceratonea	Locust bean
Locust bean	South Europe, Africa, Mediterranean area	Ceratonea	Locust bean
Locust kernel	South Europe, Africa, Mediterranean area	Ceratonea	Locust kernel
Lupogum	South Europe, Africa, Mediterranean area	Ceratonea	Locust bean
Luposol	South Europe, Africa, Mediterranean area	Ceratonea	Locust bean
M			
Mahua	India	Bassia	Indian gum
Mangrove	North and South America	Rhizophora	Ghatti substitute
"Marrons et bois"	Africa	Acacia	Arabic
Mesquite	United States, Mexico, South America	Prosopis	Arabic substitute
Mimosa	West Indies, South America	Mimosa	Tragacanth substitute
Mogador	Africa	Acacia	Arabic
Moringa	India	Moringa	Karaya substitute
Morocco	Africa	Acacia	Arabic
O			
Ondurman	Egypt	Acacia	Arabic
P			
Peach	United States	Prunus	Peach gum
Pearl moss	Europe, United States, Nova Scotia	Seaweed	Irish moss
Persian tragacanth	Iran (Persia)	Astragalus	Tragacanth
Pharmagel	United States	Protein	Gelatin
Pigwrack	Europe, United States, Nova Scotia	Seaweed	Irish moss
Plantago	Mediterranean area	Plantago	Psyllium
Plum tree gum	India	Prunus	East Indian gum
R			
Ritha	East Indies	Sapindus	Ghatti substitute
Rocksalt moss	Europe, United States, Nova Scotia	Seaweed	Irish moss
Rubigum	South Europe, Africa, Mediterranean area	Ceratonea	Locust bean

Table 45—*Continued*

Name	Place of Origin	Type	Present Day Classification
S			
Seaweed isinglass	Japan	Seaweed	Agar
Saghalien	Japan	Seaweed	Agar
Salabreida	Senegal, Africa	Acacia	Arabic
Semla	India	Sterculia	Karaya
Senaar	Central America	Acacia	Arabic
Senegal	Africa	Acacia	Arabic
Sennaar	Africa	Acacia	Arabic
Shinshu	Japan	Seaweed	Agar
Shiraz	Iran (Persia)	Anogeissus	Ghatti
Smyrna tragacanth	Kurdistan, Iran (Persia), Irak	Astragalus	Tragacanth
Siris	India	Albizzia	Arabic substitute
Soap-nut tree gum	East Indies	Sapindus	Ghatti substitute
Sonora	United States, North and South America	Prosopis	Arabic substitute
Sterculia	India	Sterculia	Karaya
St. John's bread	Africa, Mediterranean area, Europe	Ceratonea	Locust bean
Suakim	Africa	Acacia	Arabic
Sudan	Africa	Acacia	Arabic
Suleimanaya	Iran (Persia), Irak	Astragalus	Tragacanth
Sumaliland	Sumaliland	Acacia	Arabic
Sunt	Arabia, Africa	Acacia	Arabic
Swine's bread	South Europe, Africa, Mediterranean area	Ceratonia	Locust bean
Syrian	Syria	Astragalus	Tragacanth
Syrian tragacanth	Kurdistan, Iran (Persia), Irak	Astragalus	Tragacanth
T			
Talba	Sudan, Africa	Acacia	Arabic
Talca	Sudan, Africa	Acacia	Arabic
Talh	Africa	Acacia	Arabic
Talha	Africa	Acacia	Arabic
Tengusa	Japan	Seaweed	Agar
Terminalia	India	Indefinite	Indian
Thus gum	United States	Resin	Rosin

Table 45—*Continued*

Name	Place of Origin	Type	Present Day Classification
Tragacanth	Iran (Persia), Turkey, Russia, Irak, Palestine, British India, Syria	Astragalus	Tragacanth
Tragon	Africa, Mediterranean area, South Europe	Ceratonia	Locust bean
Tragasol	Africa, Mediterranean area, South Europe,	Ceratonia	Locust bean
Tripoli	Africa	Acacia	Arabic
Tunis	Africa	Acacia	Arabic
Turic	Africa	Acacia	Arabic
Turkey gum	Near East	Acacia	Arabic
V			
Vegetable isinglass	Japan	Seaweed	Agar
W			
Wattle	India, Australia, Africa, New South Wales	Acacia	Arabic
White gum (gomme blanche)	Africa	Acacia	Arabic
White leaf gum	Kurdistan, Iran (Persia), Irak	Astragalus	Tragacanth
Y			
Yokohama	Japan	Seaweed	Agar

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